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A MANUAL

OF

QUALITATIVE CHEMICAL ANALYSIS.

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A MANUAL

OF

QUALITATIVE CHEMICAL ANALYSIS

BY

WILLIAM DITTMAR,
PROFESSOR OF CHEMISTRY IN ANDERSON'S UNIVERSITY, GLASGOW.

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I AM under great obligations to my friend Mr. GEORGE CRANSTON, for the valuable assistance he has given me in preparing this Book for, and passing it through, the Press.

W. D.

ANDERSON'S UNIVERSITY, GLASGOW,
January 1876.

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INTRODUCTION.

Chemical Analysis is a branch of applied chemistry. It comprises the methods for ascertaining the composition of a given specimen of matter: and if we speak of 'qualitative' and of 'quantitative' analysis as two distinct branches of the subject, we refer to the methods, not to the problems. From this, analysis would appear to be nothing more or less than chemistry itself: and so it is—in a sense at least. In what sense, we do not now care to explain; all we desire is, at the very outset, to make the student understand that analysis is *not* an art which can be learned independently of chemistry itself. It is possible to be a fair theoretical chemist without being able to execute an analysis, but most assuredly no one can be an analyst without being a scientific chemist. There is, of course, a difference between the function of the chemical investigator and that of the analyst, which may be said to lie in the different senses in which the two understand the terms 'substance' and 'composition.' To the investigator the 'substance' he operates upon is of interest only in as far as it represents a certain species, simple or complex, of matter; and 'composition' with him means the internal organization of *that* chemical species. To the analyst the specimen itself is the subject of investigation, which, with him, is completed as soon as he has either succeeded in identifying it with this or that species duly booked in the catalogue of science; or, if it does not happen to represent any definite kind of matter, as soon as he has found out, so to say, the recipe for forming it from known chemical species. If there were a definite method, however complex, which, when carefully applied to any case that might present itself, would be sure to lead to the recipe, or to the proof that such recipe lay without the present boundaries of science, then analysis would have a standing independent of scientific chemistry. But, unfortunately, such is not the case, the fact being, that of the various questions involved in the investigation of a substance of unknown nature, just those which, logically, would have the first claims on our attention, are the ones for the solution of which we have no general methods. There is, for instance, no direct and straightforward method which would enable us to find out whether or not a given substance is chemically homogeneous, and which, if it were not so, would enable us to form some idea of the degree of complexity in its proximate composition. To this, and other general questions of a similar order, analysis, in its present state, returns no answer. All that it furnishes us with is a series of methods, each of which, on a broader or narrower basis of suppositions, enables us to answer this or that special question regarding the chemical constitution of the substance under investigation. Of the relatively general problems covered by these methods, this book takes cognisance mainly of the following two:—

1. Given a substance, what is its qualitative elementary composition? and
2. Supposing the substance to be known to consist, *substantially*, of a mixture of salt-like compounds,

what acids and bases should we require for its synthetical production?

The first of these problems will be treated more exhaustively; in the case of the second only the most important classes of salts will be taken into consideration individually; while comparatively rare acids and bases will be either entirely ignored or disposed of generically.

The book is intended for the use of students who, after they have mastered the first rudiments of chemistry, enter a laboratory to work *under the direction of a teacher*, while, at the same time, they *continue their study of theoretical chemistry.* In accordance with this supposition, the chapters in succession become more and more strictly scientific in their mode of handling the subject.

The book is divided into four Sections. The First is devoted to a series of exercises which will give an idea of analytical methods to the student who works his way through them, and thus obtains some familiarity with the operations involved in their execution. Section II. describes the properties of the most important metals, and the reactions they exhibit as such, or in one or other of their most frequently occurring states of combination. From these reactions is deduced a method for the qualitative analysis of a mixture of metals, supposing them to be given in the shape of *salts of certain acids.* Section III. treats of the non-metallic elements and their compounds, with particular regard to non-metallic acids. For each class of metalloid compounds it is shown how their metallic derivatives must be treated in order to bring the metals contained in them within the range of the methods given in II. Section IV. treats of the application of the methods in II. and III., and shows how far they are likely to be available *in the investigation of a substance of unknown nature.*

I.—EXERCISES.

What is printed in small type is meant to be read only.

THE simplest problem that can present itself in analysis is that of the substance under examination being one of those elements which can be identified by a purely qualitative observation of certain of their physical properties; such as mercury, iodine, gold, and a few others. If such elements present themselves in the shape of chemical compounds, they evidently need only to be liberated in order to be recognised as before. Such liberation may sometimes be effected by the agency of heat alone, or by the combined effects of heat and the gases of a flame, or of additional reagents. The following exercises afford examples:—

I. Place a small quantity of *mercuric* oxide, HgO, in the bottom of a 'sublimation-tube' (a tube of hard glass, closed at one end, about four inches long and a quarter of an inch wide) and heat it. The compound will break up into oxygen, which escapes, and into vapour of metallic *mercury*, which, condensing in the colder portions of the tube into metallic globules, liquid even at ordinary temperatures, is at once recognised.

II. Place a small fragment of *iodine* in a sublimation-tube, and heat it gently in a gas-flame. The iodine is volatilized and changed into an intensely violet vapour, which, in the upper parts of the tube, is condensed again into a solid, identical with the original substance.

III. Heat some *iodic anhydride* (I_2O_5) in a (not too narrow) test-tube. Violet vapours of iodine make their appearance and condense in the colder parts of the tube, while, at the same time, oxygen is liberated, which can be recognised by its property of inflaming a glowing splinter of wood.

IV. Heat, in a sublimation-tube, a small fragment of *arsenicum.* It volatilizes without previously fusing, and the vapours condense into a ring-shaped metallic-looking sublimate, firmly adhering to the glass (a 'mirror').

V. Place a fragment of '*white arsenic*' (arsenious oxide, As_2O_3), about the size of a pin's head, in the bottom of a tube of hard glass, drawn out at one end, drop into the tube a splinter of charcoal shaped so as to stop up the conical part, and heat, first the charcoal, until it is red hot, and then the arsenic, so that its vapours are driven through the heated charcoal. The charcoal (substantially consisting of carbon, C) takes away the oxygen of the compound, and the liberated metallic arsenic is deposited at some distance above the charcoal in the form of a mirror, precisely similar to the one produced in Exercise IV.

VI. Make a loop at the end of a thin platinum wire, heat this loop in the flame of a Bunsen's lamp, and dip it, quickly, into some powdered *carbonate of sodium* (Na_2CO_3), when some of the salt will adhere to it. Heat the salt in the outer portions of the flame; it first melts, and is then gradually volatilized; the vapours are decomposed with formation of *metallic sodium,* which imparts to the flame an intensely yellow colour. When viewed through a spectroscope, the flame is found to give a spectrum, consisting of one bright yellow line. The sodium vapours, formed in this experiment, cannot be condensed and collected; yet the *one* physical property referred to is sufficient to identify the metal with perfect certainty. What is here stated for carbonate of sodium holds good also for most of the other salts of that *metal.*

VII. Repeat experiment VI., only substituting for carbonate of sodium, successively, a salt of

a *b* *c* *d* *e*
Lithium | Potassium | Strontium* | Barium* | Thallium

The most convenient salts for this purpose are, respectively, the

Carbonate | Carbonate | Sulphate | Chloride | Chloride

In each case the flame will assume a colour characteristic of the *metal;* the colours are, respectively,

Crimson | Violet | Crimson | Yellowish Green | Pure Green

Examine each flame with the spectroscope; and satisfy yourself that the spectra agree with the diagrams in Roscoe's 'Lessons in Elementary Chemistry.'

VIII. Heat a small quantity of *calomel* ($HgCl$) in a sublimation-tube. It is volatilized and yields a sublimate identical with the original substance.

IX. Heat, in a sublimation-tube, a mixture of *calomel* with about three times its bulk of *carbonate of sodium.* A sublimate of metallic mercury is obtained. The chlorine of the calomel remains in the residue as chloride of sodium.

X. Mix a small quantity of *oxide of copper* (CuO) with two or three times its bulk of *carbonate of sodium*, and heat the mixture on charcoal, by means of a *blow-pipe*, in a *reducing flame.* (By a 'reducing flame' is understood a flame containing an excess of combustible gas, *i.e.* more gas than can be burned by the air in it. As long as a blow-pipe flame is luminous, however slightly, it has reducing properties.) After some minutes' heating, break off the fused mass along with those parts of the charcoal which are impregnated with the 'flux,' and triturate the whole in an agate mortar, first with one drop of water, then with more, and lastly, pour off all that does not readily subside in the water. Small flattened particles of metallic copper will be obtained, possessing the characteristic colour of that metal.

---

* In case of Barium and Strontium a *hair-fine* platinum wire must be used, in order to maintain a temperature sufficient for the volatilization of the compound.

XI. Repeat Exercise X. successively, with (*a*) oxide of *iron*, (*b*) oxide of *cobalt*, (*c*) oxide of *nickel*, instead of the copper compound. You will obtain, in each case, the respective metal in the shape of a heavy grey powder, devoid, on account of its relative infusibility, of metallic lustre, but endowed with the property, characteristic of the three metals, of being attracted by a magnet. When brought in contact with a magnetized penknife, the metallic particles stick to the blade and can be lifted out of the mortar as a coherent lump. To show that it is not the water which cements the particles of metal together, dry them at a gentle heat over a gas flame, then remove them from the blade by letting the latter pass through between your thumb and forefinger, and then again touch them with the point of the knife. They will rise up and stick to it and one another, forming a beard-like cluster of filaments. This property of being attracted by a magnet combines iron, nickel, and cobalt into a genus, and enables them to be distinguished from all other metals. How the three metals may be distinguished from one another will be shown in Exercise XIII.

XII. Fuse on to the end of a platinum wire, which has been previously bent into a loop (comp. Ex. VI.), a small quantity of *borax*, and heat the salt until it becomes a transparent colourless globule ('a borax bead'). Place on this bead a very little *binoxide of manganese* (MnO_2), and then expose it to the very tip of a blowpipe flame containing an *excess of air* (an 'oxidizing flame.' Such a flame is produced by placing the nozzle of the blowpipe deep into the gas flame and then blowing rather hard, so that a non-luminous conical flame is produced; *only* the tip of the flame is *sure* to contain an excess of oxygen). The oxide of manganese dissolves in the borax and forms a bead, which, after cooling, appears violet, the colour being due to a compound of boracic acid Bo_2O_3 with the oxide Mn_2O_3. Now heat the bead in a reducing flame (comp. Ex. X.), taking care that the bead is *entirely enveloped* in the flame. If heated in this manner for a sufficient time, the bead, after cooling, appears *colourless*, containing now a compound of boracic acid with the oxide MnO. The bead, when again heated in an oxidizing flame, reassumes its original violet colour, and may then be decolorized again by a reducing flame, and so on.

XIII. Repeat Exercise XII., substituting, successively, some oxide of (*a*) *cobalt*, (*b*) *nickel*, (*c*) *iron*, (*d*) *copper*, (*e*) *molybdenum*, for the peroxide of manganese. The effect will be as follows :—

COLOUR OF BORAX BEAD WHEN PRODUCED IN

	THE OXIDIZING FLAME	THE REDUCING FLAME
Cobalt	Intensely blue	Intensely blue
Nickel	Reddish, very faint after cooling	Grey from finely divided reduced metal. On continued blowing the metal agglomerates, leaving a clear bead[*]
Iron	Hot: yellow Cold: colourless or pale yellow	Bottle green
Copper	Green; after cooling blue	Brown-red, and opaque[*]
Molybdenum	Yellow in the heat; colourless when cold	Dark-brown

Experiments like those above described are called 'tests in the dry way;' they frequently, with little loss of time and trouble, give decisive results. They are, however, not so generally, and not to the same extent systematically applicable as those to which we shall now turn our attention, namely, the '*tests in the wet way*,' wherein the substance under examination is first dissolved in an appropriate 'solvent,' and its solution then examined by acting on it with substances ('Reagents'), the chemical nature of which is known.

---

[*] The reduction succeeds best on addition of some oxide of tin.

XIV. Take an aqueous solution of *hydrochloric acid* (HCl) and add to it *caustic potash*, KHO (solution), until the mixture no longer changes the colour of violet litmus paper. ('Neutralize hydrochloric acid with caustic potash.') Experience has shown that this point is reached as soon as the hydrochloric acid and the potash are mixed in the proportion of 'HCl' (36·5 parts) to 'KHO' (56 parts). Evaporate the solution to dryness; the residue is chloride of potassium (KCl,) what goes off is water only (H_2O.)—$KHO + HCl = KCl + HHO$. In this experiment the hydrochloric acid might be replaced by many other substances, for instance, by sulphuric acid, nitric acid, etc. etc., with a perfectly analogous result. These substances are called 'acids.' The caustic potash might also be replaced by a great number of other compounds, chiefly metallic oxides and hydrates; only in case of many metallic oxides the resulting compound would still colour violet litmus paper red. There would, however, always be a union of the hydrochloric acid with a definite quantity of the oxide, attended with the formation of water and of a compound containing the chlorine of the hydrochloric acid and the metal of the oxide. All substances which, in the above process, are capable of playing the part of the caustic potash, are called 'bases.' The product formed by the union of an acid with a base (with elimination of water) is called a 'salt.'

XV. Dissolve the chloride of potassium obtained in Example XIV. *in the least* quantity of water, and add to the solution two or three times its volume of fuming hydrochloric acid. A crystalline precipitate is produced, which, from the mode of its formation, one might expect to have resulted from the union of 'KHO' with more hydrochloric acid than 'HCl;' perhaps with two or three times that quantity.

This, however, is not the case; the precipitate is pure chloride of potassium, as can be shown by collecting and drying it on a porous tile, repeatedly washing it with a minimum of water, and always allowing the solution to be sucked up by a tile, when at last a salt perfectly neutral to litmus paper will be obtained.

XVI. Measure out half a test-tube full of a moderately dilute (say a 10 per cent.) solution of caustic potash, add to it, out of a graduated cylinder, of a solution of *tartaric acid*, until it is exactly neutralized, and note the volume of acid used. Evaporate the solution to dryness at a gentle heat. The residue is 'normal tartrate of potassium,' a white salt, very easily soluble in water.

XVII. Redissolve in water the normal tartrate obtained, and add to it as much tartaric acid as it already contains. A colourless crystalline precipitate will be formed, consisting of 'acid tartrate of potassium,' a salt very difficultly soluble in water, and also otherwise easily distinguished from the product obtained in XVI.

Tartaric acid is $(C_4H_4O_6)HH$.

Normal tartrate of potassium: $(C_4H_4O_6)KK = (C_4H_4O_6)HH + 2KHO - 2H_2O$.

Acid tartrate of potassium: $(C_4H_4O_6)HK = (C_4H_4O_6)HH + 1\ KHO - 1H_2O$.

XVIII. Measure out two equal volumes of a solution of tartaric acid. Saturate the one with caustic potash, the other with caustic soda ($NaHO$); mix the two solutions, evaporate to a small bulk, and allow to cool. If the liquid has been sufficiently concentrated, it will deposit beautiful crystals of a *chemical* compound, not a mere mechanical mixture, of the tartrates of potassium and sodium: $(C_4H_4O_6)KNa.4H_2O = \frac{1}{2}(C_4H_4O_6K_2 + C_4H_4O_6Na_2) + 4H_2O$.

We see that the quantity of tartaric acid represented by '$C_4H_6O_6$' contains two parts of hydrogen (H_2) which can be separately replaced by K or Na with formation of definite chemical compounds. The hydrogen in hydrochloric acid (HCl) is *not* divisible in this way; hence hydrochloric acid is called a *monobasic* and tartaric acid a *dibasic acid.* Examples of other monobasic acids are: Nitric HNO_3, acetic $HC_2H_3O_2$, hydrobromic HBr, hydriodic HI, benzoic $HC_7H_5O_2$; of dibasic ones: sulphuric $HHSO_4$, succinic $HHC_4H_4O_4$, oxalic HHC_2O_4, hydrosulphuric HHS. The terms 'tribasic,' 'tetrabasic' acid, etc., will now be easily understood without further explanation. Phosphoric acid ($HHHPO_4$) is an example of a tribasic acid.

XIX. Neutralize a quantity of dilute *sulphuric acid* with a solution of *hydrate of barium* (BaH_2O_2) ('baryta-water'). Neutral sulphate of barium ($BaSO_4$) is formed as a heavy white precipitate, insoluble in water and dilute acids. $BaH_2O_2 + H_2SO_4 = BaSO_4 + 2H_2O$.

XX. Saturate one volume of dilute sulphuric acid with baryta-water, then add another volume of acid. The same compound $BaSO_4$ is obtained, as in the case of an exact saturation, the second half of the sulphuric acid remaining in solution unchanged. We see that baryta behaves to sulphuric acid just as caustic potash does to hydrochloric, hence it is called a 'di-acid' base. Towards monobasic acids, *e.g.* HCl, baryta behaves exactly like potash or soda.

XXI. Dissolve some *acetate of lead* ('sugar of lead') in water, and add to the solution dilute *sulphuric acid.* A heavy white precipitate is formed, consisting of *sulphate of lead*, $PbSO_4$, acetic acid $HC_2H_3O_2$ being at the same time set free, which remains in solution along with that part of the sulphuric acid, or with that part of the acetate of lead which was present 'in excess,' *i.e.* over and above the quantity actually required in the process: $Pb(C_2H_3O_2)_2 + H_2SO_4 = PbSO_4 + 2H(C_2H_3O_2)$.

XXII. In a solution of *acetate of lead*, mixed with a few drops of acetic acid, suspend a strip of *metallic zinc*, and allow the whole to stand for some hours. The lead contained in the salt is gradually but at last completely precipitated in the metallic state,* and for every 103·5 parts of lead thus eliminated 32·5 parts of zinc pass into solution. If the process is allowed to go on, until the whole of the lead is precipitated (*i.e.* until a few drops of the liquid taken out no longer give a precipitate with sulphuric acid), the solution contains only acetate of zinc, which, after sufficient concentration of the liquid in the heat, separates out on cooling in colourless laminæ of the composition, $Zn\ (C_2H_3O_2)_2\ 3H_2O$.

---

* *As a beautiful arborescence* on and above the zinc ('Saturn's tree').

The same salt can be produced by dissolving zinc in a hot mixture of acetic acid ($C_2H_4O_2$) and water and evaporating to crystallization; 32·5 parts of zinc, in this case, eliminating one part of hydrogen gas. Acetate of lead can be prepared from acetic acid, by dissolving in a mixture of the latter with water the proper quantity of *oxide of lead;* 111·5 parts of oxide (containing 103·5 of metallic lead) eliminating nine parts of water, containing one part of hydrogen. Both the lead and the zinc acetate, when distilled with *sulphuric acid*, give sulphate and a distillate of acetic acid.

It follows, from what has been stated, that the three acetates here considered contain a common constituent, of which a certain quantity (the quantity '$C_2H_3O_2$') is combined,

In the case of acetic acid, with 1 part of hydrogen = 'H'
„ acetate of zinc, „ 32·5 parts of zinc = ½ 'Zn'
„ „ lead, „ 103·5 parts of lead = ½ 'Pb'

We also see that the three compounds can be mutually converted into one another, by the substitution of one for another

of the quantities H, ½ Zn and ½ Pb
i.e. 1, 32·5 and 103·5 parts.

Hence, in the reactions here considered, the quantities named of the three elements are said to be 'equivalent' to one another, each to each. Chemists not unfrequently speak of 'the equivalent' of an element or radicle* as being so and so much, *i.e.* they apparently attach to the word equivalent an *absolute* meaning. Such statements, however, are always tacitly understood to refer to a certain set of reactions, and by *the* equivalent of the element or radicle is meant that quantity which, in *these reactions*, is equivalent to one part of hydrogen.

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* 'Radicle = Group of elements associated with one another in certain proportions, which group, in this or that set of reactions, remains unchanged.

XXIII. (*a*) Dissolve a small quantity (a few decigrammes) of metallic copper in nitric acid, completing the process, if necessary, by heating. The metal is converted into a blue solution of nitrate of copper ($Cu(NO_3)_2$) with evolution of nitric oxide NO, a gas which is colourless in itself, but in contact with air is converted into reddish-brown vapours of peroxide of nitrogen NO_2. Evaporate some of the solution to dryness in a porcelain basin: a blue residue of nitrate is left which, on continued heating, loses nitric acid, and is at last converted into oxide of copper (CuO), a black mass insoluble in water. Dissolve the *oxide of copper* in warm hydrochloric acid. A *green* solution of chloride of copper, $CuCl_2$, is produced. Evaporate the green solution to a small bulk, so as to expel the greater part of the excess of acid, dilute with three or four volumes of water, and add a piece of *metallic zinc:* metallic *copper* is precipitated, and a part of the zinc passes into solution as chloride. $CuCl_2 + Zn = Cu + ZnCl_2$.

To some of the blue solution of nitrate of copper add about once or twice its volume of hydrochloric acid: the liquid becomes *green,* a part of the nitrate being changed into chloride. $Cu(NO_3)_2 + 2HCl = CuCl_2 + 2HNO_3$.

(*b*) Dissolve a few decigrammes of pure metallic *silver* in warm dilute nitric acid. Nitric oxide is evolved and a colourless liquid produced, which, after evaporation to dryness at a gentle heat, leaves colourless crystalline nitrate of silver, $AgNO_3$, which, when cautiously heated in a sand-bath, fuses without decomposition. After cooling, dissolve the nitrate of silver in water, and into a part of the solution drop a piece of stout copper wire: metallic silver is precipitated, while copper passes into solution as nitrate. $2AgNO_3 + Cu = Cu(NO_3)_2 + Ag_2$. To the rest of the solution add, drop by drop, hydrochloric acid (shaking violently after each addition) as long as there is a precipitate formed; the silver is completely precipitated as chloride ($AgCl$); the solution contains nitric acid, and the excess of hydrochloric acid. $AgNO_3 + HCl = AgCl + HNO_3$. Wash the chloride of silver by decantation with water, and to the magma of precipitate and water add a few drops of hydrochloric acid and a piece of metallic zinc. After a few hours' standing, the chloride will be converted into metal; the solution will contain chloride of zinc. $2AgCl + Zn = Ag_2 + ZnCl_2$. Pick out what is left of the piece of zinc, boil the precipitate with dilute sulphuric acid (to dissolve traces of zinc precipitated on its surface), and wash, by decantation, with hot water. The silver thus obtained forms a dull yellowish-grey powder, which, when rubbed with the blade of a knife, acquires metallic lustre, and when heated on charcoal with a blowpipe-flame, readily fuses together into a globule, exhibiting the characteristic properties of the metal.

(*c*) Treat a *silver coin* with dilute nitric acid (aiding the action by gentle heating when necessary) until it is completely dissolved. Silver coins are made of an alloy of silver and copper, but not unfrequently contain also traces of gold. The silver and copper dissolve as nitrates, the gold, if present, remains as a heavy black powder, insoluble in even hot nitric acid. Of the solution obtained take

(1) A part and evaporate it to dryness in a porcelain basin placed on a sand-bath, heat the mixed nitrates to fusion, and continue heating until all the (green) basic nitrate of copper, which is first formed, is completely reduced to (black) oxide. Treat the residue with warm water, and filter. The residue on the filter is oxide of copper, the solution contains nitrate of silver, which, if the heating

process was properly conducted, is perfectly free from copper salt. The oxide of copper, however, almost invariably contains a little metallic silver, which can be rendered visible by dissolving away the oxide of copper in warm dilute sulphuric acid. This is a convenient process for *preparing* nitrate of silver, but not an exact method for separating the two metals.

(2) Dilute the rest of the nitric solution of the coin with water to about fifty times the weight of the metal it contains, filter, if necessary, and put it into a bottle capable of holding from four-thirds to twice the bulk of liquid. Add now a small quantity of hydrochloric acid (presumably insufficient for the complete precipitation of the silver present), shake up violently until the chloride of silver precipitate has coagulated and the liquid lost its milky appearance, allow to settle, and by addition of one drop of hydrochloric acid to the clear supernatant fluid, see if there is any silver left in the solution. If so, add more hydrochloric acid, shake up, test again, and so go on until, as nearly as possible, the exact quantity of hydrochloric acid necessary for the complete conversion of the silver into chloride has been added. Wash the precipitate with cold water (by decantation) until the whole of the copper has been removed, *i.e.* until the last wash-water is no longer coloured by ferrocyanide of potassium. Transfer then the chloride of silver to a short-necked flask, provided with a well-fitting cork, dissolve the precipitate in strong aqueous ammonia, slide in some pieces of *stout* sheet copper (about five times the weight of the coin), put in the cork, and allow the whole to stand until the blue colour of the mixture, which makes its appearance immediately after the introduction of the copper, after having for some time increased, begins to diminish in intensity. The silver is now completely reduced to the metallic state and precipitated, the chlorine having been taken away by the copper and converted, for the greater part into a blue compound

of *cupric chloride* and ammonia ($CuCl_2 + xNH_3$), the rest into a colourless compound of *cuprous chloride* and ammonia ($CuCl + yNH_3$), both of which remain dissolved in the liquid. If atmospheric oxygen be completely excluded, the precipitation of the silver is completed as soon as $Cu\frac{1}{2} = 31{\cdot}7$ parts of copper have dissolved for every $AgCl = 143{\cdot}5$ parts of chloride of silver employed, the composition of the mixture (apart from what is left of the copper strips) then corresponding to the equation :—

$$AgCl + \tfrac{1}{2}Cu = Cu_{\frac{1}{2}}Cl + Ag \text{ .... I.}$$

If the mixture is allowed to stand, its colour gradually disappears, the (blue ammoniacal) cupric chloride being gradually reduced to (colourless ammoniacal) cuprous chloride, thus :—

$$Cu_{\frac{1}{2}}Cl + Cu_{\frac{1}{2}} = CuCl \text{.................... II.}$$

So that, finally, the state of matters is the same as if from first to last this process had been going on :—

$$AgCl + Cu = Ag + CuCl \text{ .... III.}$$

If the colourless liquid (containing its copper as $CuCl$) is added to an ammoniacal solution of *chloride of silver*, the silver is at once reduced to the metallic state, the chlorine passing to the cuprous and converting it into cupric chloride :—

$$CuCl + AgCl = CuCl^2 + Ag \text{ .... IV.}$$

From this it at once appears that equation I. cannot be looked upon as a true theory of the process up to (although it correctly formulates the distribution of matter at) the moment it refers to. Because, obviously, as soon as some cupric chloride is formed by reaction I., this cannot help undergoing reaction II., and being thereby reduced to cuprous chloride, which will then act on chloride of silver according to equation IV. with formation of cupric chloride, which, after having been reduced by the copper-strips, again attacks some of the chloride of silver according to IV., etc. etc. In other words : of the copper which takes part in the process, only a part reduces chloride of silver directly ; the rest does so only after having previously passed into the state of cuprous chloride. That this second part must be greater than the first does not require to be pointed out. Remembering that the chloride of silver we used originated from the reaction $AgNO_3 + HCl = AgCl + HNO_3$, we may look upon the processes resulting in I and III. respectively, as two modes of converting chloride of hydrogen into chloride of copper.

In the one (I.) HCl is finally converted into Cu_2Cl, in the other (III.) HCl passes into CuCl. In I. $\frac{Cu}{2} = 31·7$, in III. $Cu = 63·4$ parts of copper are 'equivalent' to one part of hydrogen. (Compare Exercise XXII.

After removing mechanically what is left of the copper, decant the copper solution and wash the silver, first, with dilute ammonia in presence of air (to dissolve out any trace of copper that may be left), and then repeatedly with water, until the last trace of copper is removed, *i.e.* until the decanted liquid no longer becomes blue in contact with air, and after acidification with acetic acid, gives no colouration with ferrocyanide of potassium. The metallic silver, obtained in this process, forms a very fine powder, (generally) devoid of metallic lustre. When heated to redness (in a porcelain crucible) it shrinks and cakes together, and then presents the aspect of a metal. To prepare perfectly pure *nitrate of silver* (a reagent constantly required in analysis), dissolve the ignited metal in nitric acid and evaporate to dryness. If the salt should contain a trace of copper, this can easily be removed according to process (1).

XXIV.* *Recapitulation.* It was shown (in XXIII.) that a solution of *nitrate of silver*, when mixed with one of hydrochloric acid, gives a precipitate of chloride of silver and a solution containing, besides the excess of substance or reagent used, the nitric acid previously combined with the elements of oxide of silver Ag_2O in the decomposed part of the nitrate of silver. The process goes on according to the equation:

$$AgNO_3 + HCl = AgCl + HNO_3 \text{ .... } (1)$$

If instead of *hydrochloric acid* (chloride of hydrogen, HCl) we use chloride of *potassium* KCl, a perfectly similar reaction is observed, only instead of a solution of nitric acid (nitrate of hydrogen HNO_3) there is formed one of nitrate of *potassium*, KNO_3. (2).—Any other soluble chloride, RCl may be substituted for the two named, we always have :—

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* Students who, on cursorily reading over this chapter, find it hard to understand, may postpone its study until they are a little more familiar with chemical reactions.

$AgNO_3 + RCl = AgCl + RNO_3$ .... (3)

If in reaction (2) we substitute for the *chloride* the carbonic acid salt ('carbonate') of potassium K_2CO_3, we observe an analogous reaction ; only the precipitate this time consists of *carbonate* (Ag_2CO_3) (instead of chloride) of silver.

$AgNO_3 + \frac{1}{2}(K_2CO_3) = Ag(CO_3)_{\frac{1}{2}} + KNO_3$ .... (4)

Caustic potash (hydrate of potassium KHO) and nitrate of silver also precipitate each other, in this way :—

$AgNO_3 + KHO = AgHO + KNO_3$ .... (5)

The hydrate of silver, however, at once breaks up into oxide of silver Ag_2O (a dark brown precipitate) and water : $AgHO = \frac{1}{2}Ag_2O + \frac{1}{2}H_2O$.

(According to XXI.) a solution of *acetate of lead* and one of *sulphuric acid* give a precipitate of *sulphate of lead* and a solution of acetic acid :—

$Pb(C_2H_3O_2)_2 + H_2SO_4 = PbSO_4 + 2H(C_2H_3O_2)$ (6)

Substituting the potassic for the hydric salt of sulphuric acid we have :—

$Pb(C_2H_3O_2)_2 + K_2SO_4 = PbSO_4 + 2K(C_2H_3O_2)$ (7)

Other soluble sulphates behave similarly, *e.g.*

$Pb(C_2H_3O_2)_2 + CuSO_4 = PbSO_4 + Cu(C_2H_3O_2)_2$ (8)

(According to XIX.) solutions of *hydrate of barium* and *sulphuric acid* give insoluble *sulphate of barium* and *water* :—

$Ba(HO)_2 + H_2SO_4 = BaSO_4 + 2H_2O$ .... (9)

Substituting *chloride* for hydrate of barium we have :—

$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$ .... (10)

In both reactions the sulphuric *acid* can be replaced by other soluble *sulphates* with a perfectly similar effect, for instance :—

$BaCl_2 + K_2SO_4 = BaSO_4 + 2KCl$ .... (11)

and

$Ba(HO)_2 + Na_2SO_4 = BaSO_4 + 2NaHO$ .... (12)

In looking over these reactions we find they are all analogous to one another in so far as, in each case, there are acting upon each other two compounds (belonging to the categories of 'acid,' 'base,' or 'salt'), and that the action consists in the cross-exchange of a constituent of the one compound for a constituent of the other, with formation of two new substances. Such reactions are called 'double decompositions.' We also see (by comparing reactions (1) and (2), or (6) and (7)) the analogy in the double decompositions of hydrochloric *acid* and sulphuric *acid* with those of *chlorides* and *sulphates* respectively. In comparing (9) with (10), and (11) with (12), we observe the similarity, in their behaviour to sulphates, of *hydrate* and *chloride* of barium. Similar facts have been observed in countless other analogous reactions. 'Free acids' and 'free bases,' in their ordinary double decompositions, behave like metallic salts, the *acids* like salts of the *'base' water* (or of the 'metal' *hydrogen*); the *bases* like salts of the *'acid' water;* the residue OH in hydrates (or $O_{\frac{1}{2}}$ in oxides) playing the part of the residue 'Cl in a *chloride*, or of the residue $\frac{1}{2}SO_4$ in a *sulphate*.'

Most of the reactions taken advantage of in analysis are double decompositions of salts by salts, or acids or bases. We shall, therefore, here state some general facts which have been made out regarding such reactions, and the knowledge of which often enables one to foresee their result. In doing so, we shall use the word 'salt' in a wider sense, so as to let it include acids and basic hydrates, and, consequently, the word 'metal' as including 'replaceable hydrogen.'

If the solution of any salt RA * is mixed with that of another salt R′A′ (where RA and R′A′ stand for the respective formulæ, R and R′ being the metallic, and A and A′ the acid residues, and R′ and A′ are supposed to be different from R and A respectively) there always *is* double decomposition, which, however, in no case takes place instantaneously, but always proceeds gradually, at a rate which in general changes as the action progresses. But the new salts R′A and RA′ are no sooner formed than they also commence mutually decomposing each other into the original salts RA and R′A′ at a rate which evidently must increase, as the number of molecules of R′A and RA′ formed becomes greater.

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* **RA is meant to represent the formula of a salt, containing the metal R, and the acid radicle A.**

What this ultimately leads to depends chiefly on the nature of the two new salts produced.

If both of the two salts R′A and RA′ are absolutely soluble (*i.e.* are such that at any imaginable stage of the reaction the quantities produced could remain permanently dissolved in the liquid as it would be at that stage), the two reactions expressed by the equation $RA + R'A' = R'A + RA'$ will both go on *ad infinitum*, but sooner or later there will be reached a point when the two reactions exactly compensate each other, and the composition of the liquid no longer changes.

Suppose, now, one of the products formed (say R′A) is absolutely *insoluble*, *i.e.* such that even the least quantity of it, after being once formed, cannot remain permanently dissolved. Then, however short a way the process may go at first, the quantity of R′A produced will separate out (as a precipitate, or as gas evolved) and be withdrawn from the sphere of action. The forward reaction will again predominate over the inverse one, an additional quantity of R′A be produced and eliminated, and this will go on until the whole of the potentially present quantity of R′A is actually produced and separated out: the process will go on to the end.

If R′A is only relatively insoluble, it is far more difficult to predict even the phenomenal result of the reaction. It is however easily understood, that, whenever the quantity of R′A potentially present (call it $(1 + n)$ Q) exceeds the quantity Q, which—supposing it to be actually formed—would bring the liquid into the condition of a solution saturated with R′A, a part of the excess in Q will, in general, separate out. The greater n, the greater the probability of a precipitation of R′A setting in at all, and, if it does, the greater a fraction of the quantity nQ will ultimately be precipitated.

That the *whole* of that quantity will not be separated out follows at once from what was stated above with regard to soluble products.

All this applies to gases as well as to solid or liquid precipitates. The case of a gaseous product, however, offers this peculiarity, that if the gas is produced, besides relatively *non-volatile* compounds, it can, as a rule, be *completely* expelled by a sufficient increase of temperature, or, if necessary, by evaporation, and the reaction thus be *forced* to go on to the end.

Examples.—(A) *Formation of soluble products.*—(1) A concentrated (blue) solution of *sulphate* of copper, when mixed with hydrochloric acid, assumes the characteristic *green* colour of cupric *chloride.* $CuSO_4 + 2HCl = CuCl_2 + H_2SO_4$. But, even if more than 2HCl be added for every $1CuSO_4$, some of the latter salt remains undecomposed, the mixture contains, besides $CuCl_2$ and H_2SO_4, also $CuSO_4$, and HCl. (2) A solution of *ferric chloride* (*yellow*) when mixed with a solution of *sulphocyanide of potassium* (*colourless*), exhibits the *red* colour characteristic of *ferric sulphocyanide.* (3) A mixed solution of *chloride of potassium* and *nitrate of sodium* contains, besides these salts, also *chloride of sodium* and *nitrate of potassium.* In this case there is no visible evidence of decomposition, but yet we have good reasons for assuming that an exchange of K for Na has actually taken place. We know, for instance, that two solutions prepared, the one by dissolving the exact quantities KCl and $NaNO_3$, the other by dissolving the exact quantities NaCl and KNO_3 in equal quantities of water, are absolutely identical in all their chemical and *physical* properties. How far, in reactions like this, the double decomposition goes before it is compensated by the inverse reaction, is a problem which has not yet received a general solution. We know only that in particular cases, the one reaction to such an extent outweighs the other that, practically, the former can be supposed to go on alone. Thus, for instance, the reactions of 'strong' acids (such as sulphuric, nitric, hydrochloric, oxalic) on soluble bases (such as potash, soda, baryta) are practically non-reversible, or in other words, salts formed by the union of strong acids and strong soluble bases are not at all decomposable by water. (4.) A solution of *sulphate of zinc* $ZnSO_4$ in even very dilute sulphuric acid is not visibly affected by *sulphuretted hydrogen* H_2S. A solution of *acetate* *of zinc* in very dilute acetic acid is (by an excess of the same reagent) completely decomposed into *sulphide of zinc* (which separates out as a white precipitate) and into *acetic acid.* A mixture of even an acid solution of *sulphate of zinc* with a large excess of *acetate of soda* (*i.e.* with considerably more than $2NaC_2H_3O_2$ for every $ZnSO_4$) behaves to sulphuretted hydrogen like a solution of acetate of zinc.

Examples of partial precipitation.—A solution, saturated in the heat, of KCl parts of *chloride of potassium,* if mixed with a similarly conditioned solution of $NaNO_3$ parts of *nitrate of sodium,* deposits, on cooling, crystals of *nitrate of potassium,* the solution contains *chloride of sodium,* with more or less of the two salts originally taken. Eq.: $KCl + NaNO_3 = x(NaCl + KNO_3) + (1-x)\{KCl + NaNO_3\}$ (2) A concentrated solution of *nitrate of silver* $AgNO_3$, when mixed with one of *sulphate of sodium* Na_2SO_4 gives a crystalline precipitate of *sulphate of silver* Ag_2SO_4 and a solution, which, if the two salts were mixed in the proportion of $AgNO_3 : \frac{1}{2} Na_2SO_4$ consists substantially of one of *nitrate of sodium,* but in all cases gives the reactions also of sulphate and of silver-salt. (3) A solution of *acetate of lead,* when mixed with an excess of *hydrochloric acid,* is almost completely decomposed into *chloride of lead* (of which a part separates out as a crystalline precipitate) and into *acetic acid,* which remains in solution, but invariably the solution shows the reactions of (chloride and) lead-salt.

Examples of (practically) *complete precipitation* were given in the beginning of the paragraph. We will add the following as a case of the formation of *two* insoluble products. If the exact quantities Ag_2SO_4 and $BaCl_2$ are separately dissolved and then mixed together, there results a mixed precipitate $BaSO_4 + 2AgCl$ and a liquid consisting of pure water.

Cases of gas evolution.—(1) Almost all *carbonates* (whether soluble or —in the ordinary sense of the word—not) when treated with solutions of strong acids are completely decomposed into metallic salt (sulphate, chloride . . .) and carbonic acid; the latter, however, immediately breaks up into water and *carbonic anhydride,* which escapes as a gas. Ex.: $CaCO_3 + 2HCl = CaCl_2 + \{H_2CO_3 = H_2O + CO^2\}$. (2) All soluble and a great many of what are called 'insoluble' sulphides, when treated with the proper free acids, are decomposed with evolution of *sulphuretted hydrogen* H_2S. Ex.: $FeS + H_2SO_4 = FeSO_4 + H_2S$. (3) A solution of NaCl parts of chloride of sodium, when mixed with H_2SO_4 or more parts of *sulphuric acid,* is acted upon according to the equation $NaCl + H_2SO_4 = HCl + NaHSO_4$. Both products, however, being soluble in water, the decomposition never goes to the end. But if we separate, by continued evaporation, the water and the hydrochloric acid formed, from the non-volatile salt $NaHSO_4$

and the relatively non-volatile sulphuric acid, the whole of the potentially present hydrochloric acid is at last formed and eliminated. *Dry chloride of sodium* and *concentrated sulphuric acid* act upon each other in the same way, but much more energetically and thoroughly than in presence of water, because the gas HCl, being insoluble in concentrated sulphuric acid, is removed almost as quickly as it is formed. (4) Dry *nitrate of potash* when *heated* with excess of *concentrated sulphuric acid*, is gradually but at last completely decomposed into *bisulphate of potash* $KHSO_4$ and *vapour of nitric acid.*

The empirical laws above stated, with regard to the mutual decomposition of two salts (separately dissolved beforehand in water, etc.), can be applied to a class of reactions which are frequently carried out in analysis, viz., such double decompositions in which a relatively *insoluble* solid salt RA, by the action on it of a *solution* of another salt, R′A′ is converted into another ‘insoluble’ salt RA′ and a solution of R′A. The *possibility* of the reaction $RA + R'A' = RA' + R'A$ is easily understood: however little soluble RA may be in the solution of R′A′, a minute quantity α (RA) of it at least will dissolve, and meeting an enormous excess of R′A′, be almost completely converted into RA′, and if, under the circumstances, RA′ is to a sufficient extent less soluble than the original salt RA, a part of it is sure to separate out. There will then be room (so to say) in the liquid for another small quantity β (RA) which in its turn will dissolve, be converted into β (RA′) and be partially precipitated, and so it *may* go on. Supposing now the reaction to have gone a certain length, what are the conditions of its progressing further?

Before attempting to find an answer let us pass to a special case, taking care, however, to keep our reasoning as general as possible. Supposing we had boiled ‘$BaSO_4$’ parts of sulphate of barium, with ‘K_2CO_3’ parts of carbonate of potassium, and after so and so many minutes boiling, managed to convert 1-10th, 1-3d . . . of the ‘$BaSO_4$,’ say for the sake of generality, x $BaSO_4$ into x $BaCO_3$ (mixed of course with (1—x) $BaSO_4$) and consequently also converted the solution into one of [x (K_2SO_4) + (1—x) (K_2CO_3)].

Suppose also, for the sake of simplicity, the rates of solubility of sulphate of barium and of carbonate of barium *not* to have changed in consequence of the exchange in the solution of x (K_2CO_3) for x (K_2SO_4) (or what comes to the same, suppose these rates to be independent of x). The probability then of the reaction $BaSO_4 + K_2CO_3 = BaCO_3 + K_2SO_4$ progressing, evidently is the greater, the greater—in the small quantity of sulphate of barium, which next passes into solution—the ratio of what is converted into carbonate to what remains in the state of sulphate. But this ratio is, as we know, the greater, the greater (1—x) or the greater $\frac{1-x}{x}$; in other words: the probability of the transformation of sulphate into carbonate of barium progressing is the less, the further it has already progressed. Quite in accordance with this, experience shows, that the decomposition comes to a stop as soon as the ratio in the liquid of weight of sulphate of potash: weight of carbonate of potash has reached a certain limit value k (which lies somewhere below the number 3). If instead of taking $1K_2CO_3$ for every $1BaSO_4$ we employ an excess of the former, *e.g.* $(1 + \Delta)\ K_2CO_3$ then the greater Δ, the greater a proportion of the sulphate of barium started with is converted into carbonate. Similar relations hold with other processes analogous to the one just considered; only in many cases, even if only $1R'A'$ is used for $1RA$, the decomposition $RA + R'A' = RA' + R'A$ is completed *before* the limit value 'k' is reached, while again in other cases the 'k' is practically $= 0$, so that the decomposition does not set in at all.

Examples.—Precipitated *chromate of silver* (a red salt, soluble in about 6000 parts of water), if treated with a solution of *chloride of sodium* is decomposed with formation of (practically insoluble) chloride of silver and a (yellow) solution of chromate of sodium, thus: $Ag_2CrO_4 + 2NaCl = 2AgCl + Na_2CrO_4$. In this case $k = \infty$, *i.e.* in whatever proportions the two salts may have been taken, the whole of the potentially present chloride of silver is actually produced. (2) Recently precipitated *chloride of silver*, when treated with the solution of a slight excess of *iodide of potassium*, KI, is *completely* converted into a precipitate of iodide of silver: $AgCl + KI = AgI + KCl$. In this case also $k = \infty$, although both silver salts, even the chlorides, are almost insoluble in the liquid. (3) $SrSO_4$ parts of *sulphate of strontium*, when boiled with a solution of (considerably) more than K_2CO_3 parts of *carbonate of potash*, are completely converted into $SrCO_3$. (4) Precipitated *carbonate of calcium* $CaCO_3$ when treated with a solution of *caustic potash* KHO in at least ten times its weight of water, is not changed. Here, with regard to the reaction $CaCO_3 + 2KHO = Ca(HO)_2 + K_2CO_3$, $k = 0$. If, however, a more concentrated solution of potash be taken, the decomposition *does* take place, k being the greater, the greater the concentration of the liquid.

XXV. *Preparation of sulphuretted hydrogen.*—Place into a gas-evolution bottle from 30 to 50 grammes of fused *sulphide of iron*, FeS, and add, through the funnel tube, commercial hydrochloric acid of about 20%: the acid readily acts on the sulphide, changing the iron into chloride $FeCl_2$

which dissolves in the water, while the sulphur is converted into gaseous sulphuretted hydrogen, which escapes. (Compare page 23.) When the gas-evolution slackens, add some more acid, and so go on until a sufficiency of gas is produced. Pass the sulphuretted hydrogen, first through a tube loosely filled with cotton wool, in order to free the gas from small particles of liquid mechanically carried over, and then through distilled water contained in a phial, as long as some of it is absorbed. To see if the liquid is perfectly saturated with gas, close the mouth of the bottle, violently shake it, then turn the bottle upside down, and carefully slacken the stopper. As long as the water is not perfectly saturated, air-bubbles are sucked in ; if the point of saturation is reached, part of the liquid is forced out. When the water is completely saturated, close the phial with a cork, and preserve it for use (best with mouth turned downwards).

XXVI. *Preparation of sulphide of ammonium.*—Pass *sulphuretted hydrogen* through a measured volume, say 50 c.c. of a solution of *ammonia* (of about 10°/₀), until it is completely saturated, then add another volume (50 c.c.) of ammonia solution, mix the two liquids and keep the solution as one of '*sulphide of ammonium.*' The processes going on are represented by the following equations :— (1) $NH_3 + H_2S = NH_4.HS$. (2) $NH_4.HS + NH_4.HO = (NH_4)_2S + H_2O$. Recently prepared aqueous sulphide of ammonium is a colourless liquid, possessing a strong alkaline reaction ; when mixed with excess of any free acid it yields sulphuretted hydrogen and a clear solution of ammonia-salt ; Ex. : $(NH_4)_2S + H_2SO_4 = (NH_4)_2SO_4 + H_2S$. A solution of sulphide of ammonium readily absorbs oxygen from the atmosphere and thereby assumes a yellow colour, a part of the compound $(NH_4)_2S$ being converted into *disulphide* $(NH_4)_2S_2$. (1) $(NH_4)_2S + O = (NH_4)_2O + S$. (2) $S + (NH_4)_2S = (NH_4)_2S_2$. The *yellow* solution, when mixed with acid, gives (beside NH_4 salt and H_2S gas) a white milky precipitate of sulphur. $(NH_4)_2S_2 + 2HCl = 2NH_4Cl +$

$H_2S + S$. A slight admixture of disulphide does not interfere with most of the purposes for which the reagent is used in analysis.

XXVII. Dissolve a few centigrammes of *white arsenic* (As_2O_3) in aqueous *hydrochloric acid* and add to the solution of $AsCl_3$ thus obtained *sulphuretted hydrogen water* until the liquid, after shaking, smells strongly of the gas. Insoluble sulphide of arsenic (As_2S_3) is precipitated, hydrochloric acid goes into solution: $2AsCl_3 + 3H_2S = As_2S_3 + 6HCl$. Collect the yellow precipitate on a filter, wash it with water until the wash-water no longer contains hydrochloric acid (reddens litmus); then pour on the precipitate some sulphide of ammonium; the precipitate dissolves, being converted into a soluble double sulphide $As_2S_3\ x(NH_4)_2S$. If we acidify this solution with hydrochloric acid, the sulphide of ammonium is decomposed (*vide* supra), and the sulphide of arsenic reprecipitated.

XXVIII. Mix a solution of *nitrate of bismuth* with an excess of *sulphuretted hydrogen water:* the bismuth is completely converted into a brown precipitate of *sulphide of bismuth,* while nitric acid passes into solution. Wash the precipitate with water, and treat it with *sulphide of ammonium;* it does not at all dissolve. The filtered liquid, when acidified with hydrochloric acid, yields sulphuretted hydrogen and a solution of chloride of ammonium, mixed perhaps with more or less of a milky precipitate of sulphur, but no sulphide of bismuth is separated out.

XXIX. Dissolve a few centigrammes of *ferrous sulphate* in water acidified slightly with sulphuric acid, and add some *sulphuretted hydrogen water:* there will be no visible change. Now add an excess of *ammonia:* a black precipitate is formed, which, if a sufficiency of sulphuretted hydrogen has been used, contains the *whole* of the iron as sulphide, FeS. The same result is obtained by adding to the iron solution—instead of sulphuretted hydrogen and ammonia—a ready-made solution of *sulphide of ammonium,* the reaction corresponding in both cases to the equation : $FeSO_4 + (NH_4)_2S = FeS + (NH_4)_2SO_4$. Collect the precipitate of sulphide of iron on a filter, and add to it some dilute sulphuric (or hydrochloric) acid ; it dissolves with evolution of sulphuretted hydrogen, a solution of ferrous sulphate (or chloride) being formed.

XXX. Add to a solution of *chloride of calcium*, $CaCl_2$, first, sulphuretted hydrogen, then sulphide of ammonium : in either case there is not any visible change. Now add, to another quantity of the solution, a solution of carbonate of ammonium, and heat gently. If enough of the reagent was added, the whole of the calcium is precipitated as *carbonate* $CaCO_3$. React. : $CaCl_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_4Cl$.

XXXI. Try, successively, the action on a solution of *chloride of potassium*, first, of sulphuretted hydrogen, secondly, of sulphide of ammonium, thirdly, of carbonate of ammonium : in no case is there any visible change produced, both sulphide and carbonate of potassium being soluble in water.

The reactions described in the preceding paragraphs come out equally with *many* other salts of arsenic, bismuth, iron, calcium, and potassium than those mentioned.

XXXII. Prepare a solution containing the chlorides of *arsenic*, *bismuth*, *iron* (ferrous), *calcium*, and *potassium*, and then separate from one another these metals with the help of the reactions before given for the individual metals, *i.e.*,

(1) Dilute the liquid and pass in *sulphuretted hydrogen gas*, so as to completely precipitate the arsenic and bismuth as sulphides, wash the precipitate with water until the last washings no longer contain iron, calcium, and potassium (*i.e.* until they no longer give a colouration with sulphide of ammonium, and after evaporation in a small platinum dish, leave no residue non-volatile at a red heat). Mix the sulphides on the filter with *sulphide of ammonium*, taking care at first not to tear the paper, then pierce the bottom of the filter with a pointed glass rod, let the mixture run into a flask, and heat it gently for about five minutes, so as to

completely dissolve the sulphide of arsenic. Collect the sulphide of bismuth on a new filter, wash it with lukewarm water (always adding at the same time some sulphide of ammonium) until at last the wash-water no longer contains arsenic, *i.e.* behaves to hydrochloric acid like a very dilute solution of sulphide of ammonium. From the filtrate, mixed with the more concentrated portions of the washings, precipitate the *arsenic* (as sulphide) by acidification with hydrochloric acid, collect the precipitate on a filter, and free it from the chloride of ammonium adhering to it by repeated washing with water.

(2) To the filtrate from the arsenic and bismuth precipitate add, first, enough of ammonia to completely saturate the free hydrochloric acid it contains, then add a sufficient quantity of *sulphide of ammonium* to precipitate the whole of the *iron*, and collect the precipitate on a filter. [The filtration is considerably facilitated by adding to the mixture (if necessary) some more chloride of ammonium, gently heating and then violently shaking it.] Wash the sulphide of iron with warm water (mixed with a little sulphide of ammonium, to protect the precipitate against the oxidizing action of the atmosphere) as long as the filtrate contains any calcium and potassium (*i.e.* anything *not* volatile at a dull red heat).

(3) To the filtrate from the sulphide of iron add a sufficiency of *carbonate of ammonia*, heat it for some time, filter off the *carbonate of calcium*, and wash it with hot water.

(4) Evaporate the filtrate from the calcium precipitate to dryness: the residue contains the potassium (as chloride), along with the ammonia salts introduced as reagents. The ammonia salts are easily driven off by exposing the mixture, conveniently in a small porcelain crucible, to a dull red heat, as long as any heavy white fumes are observed to rise from the mass. The chloride of potassium remains.

(5.) In order to identify the products obtained as compounds of the *metals* they are supposed to contain, subject them, severally, to the following tests :—

(*a*) *Sulphide of arsenic.*—Boil the precipitate in a porcelain basin, with a mixture or three volumes of hydrochloric, and one volume of nitric acid. The sulphide is thereby converted into sulphur (which first separates out in flakes, and then runs together into viscid globules) and sulphuric and arsenic acids, which pass into solution. Remove the sulphur, evaporate off the bulk of the excess of reagents used, super-saturate the residual liquid with ammonia, and add *sulphate of magnesia:* there will be formed a white crystalline precipitate, consisting of *arseniate of ammonia* and *magnesia* $Mg(NH_4)AsO_46H_2O$.

(*b*) *Sulphide of bismuth.*—Boil the precipitate in a porcelain basin, with strong (fuming) hydrochloric acid, until it is dissolved with exception perhaps of a little sulphur, which may separate out. The solution contains the bismuth as chloride, $BiCl_3$. Evaporate to a small bulk, so as to expel as completely as possible the excess of hydrochloric acid left, and then pour the residue into about fifty or a hundred times its volume of water. A copious white precipitate is formed, consisting of *basic chloride of bismuth*, $BiCl_3+xBi(HO)_3$.

(*c*) *Sulphide of iron.*—Treat the precipitate with cold dilute hydrochloric acid, which should dissolve it completely into a colourless solution of ferrous chloride. (If a black residue is left, this shows that the bismuth had not been completely separated out by means of sulphuretted hydrogen.) To the ferrous chloride solution add some drops of nitric acid and boil: it will thereby be converted into a solution of *ferric chloride*, which is intensely yellow in the heat, and which, when mixed with excess of ammonia, gives a brown precipitate of ferric hydrate.

(*d*) *Carbonate of calcium.*—Treat the precipitate with *acetic acid*, so as to convert it into a solution of acetate of calcium. The solution, when moderately diluted with water and then mixed with *sulphuric acid*, remains clear. When mixed with *oxalate of ammonia* it gives a white precipitate of *oxalate of calcium.*

(*e*) *The chloride of potassium* can be identified by means of the spectrum apparatus. (See Exer. VII.) It ought to be completely soluble in water; as a rule, however, the solution is turbid from impurities out of the reagents and glass vessels used in the separations. Filter off the dregs, add *bitartrate of sodium* solution, and stir up violently. A colourless crystalline precipitate will be formed, consisting of *bitartrate of potassium.* The series of operations detailed under (1), (2), (3), and (4) separates from one another, not only arsenic, bismuth, iron, calcium, and potassium, but applies equally and with an analogous effect to the nitrates, chlorides, sulphates (and other classes of salts, but not to *all* salts) of five distinct groups of metals, of which, in this exercise, the metals named are chosen as representative members. These groups comprise respectively:—

(ARSENIC GROUP.)	(COPPER GROUP.)	(IRON GROUP.)
Arsenic	*Bismuth*	*Iron*
Antimony	Copper	Aluminium
Tin	Cadmium	Chromium
Gold	Lead	Nickel
Platinum	Mercury	Cobalt
	Silver	Manganese
		Zinc
		Uranium

(BARIUM GROUP.)	(POTASSIUM GROUP.)
Calcium	*Potassium*
Barium	Sodium
Strontium	Ammonium
	(Magnesium)

and each group, besides those enumerated, some other metals of comparatively rare occurrence.

II.—METALS.

1. In this division we propose to give the leading physical and chemical properties of metals, and their most important oxides, hydrates, and salts; and to show how each metal may be searched for and identified by dry-way tests, and by the reactions of the aqueous or acid solutions of its salts. With respect to the latter it is to be observed that these reactions, even those which are founded on the formation of compounds (say, precipitates) consisting only of the metal and elements introduced by the reagents, are not generally independent of the nature of the acid (or acids) from which the salt is derived; nor, what is more obvious, of other salts which may be present. Hence, in strictness, we ought not to speak of the reactions of 'the salts' of a metal generally, but only of that group of salts to which our reactions apply. In giving in the subsequent chapters, the 'reactions of the solutions of the salts of a metal,' we have in view chiefly the chloride, bromide, nitrate, and sulphate. Most of the reactions, it is true, are much more generally applicable, especially those founded on the formation of insoluble sulphides; but, on the other hand, there are many classes of salts to which the reactions would not apply. They would generally *not* hold for solutions of cyanides, and many other organic salts; very often not for the fluorides and pyrophosphates; and are never meant to apply to the sulpho-salts. The following instances may serve to warn the student against hasty generalizations;—

Solutions of most ordinary mercuric salts when mixed with caustic potash give a precipitate of mercuric oxide; mercuric cyanide, however, is not precipitated by the alkali. Solutions of copper salts are generally precipitated by sulphuretted hydrogen; but the solution of the double cyanide of cuprosum and potassium is not affected by sulphuretted hydrogen; ferrocyanide of potassium, although a ferrous salt, gives no precipitate with sulphide of ammonium, ammonia, or carbonate of ammonia. Ferric salts, generally speaking, when mixed with ammonia give a precipitate of ferric hydrate; but ferric tartrate is not precipitated by this reagent. A solution of fluoride of antimony gives no precipitate with sulphuretted hydrogen. These examples might be extensively multiplied.

In Division III. we shall show that all the metals existing in any given substance can, by proper processes, be converted into such salts as are within the reach of the reactions detailed in Division II.

A. COPPER GROUP.

SILVER, MERCURY, LEAD, COPPER, BISMUTH, CADMIUM (PALLADIUM).

Silver.

2. **Silver** is a white metal, soft, very malleable; specific gravity 10·5; fuses at a bright red heat (1000° C.); is not altered in pure air. When kept in fusion in air or oxygen it is not oxidized, but absorbs (up to 22 times its volume of) oxygen, which separates out as the metal begins to solidify, giving rise to the phenomenon of 'spitting.' A few parts in the thousand of copper, lead, or other foreign metals, deprive silver of this power of absorbing oxygen. It is not acted on sensibly by dilute hydrochloric or sulphuric

acid. Dilute nitric acid easily dissolves silver, changing it into nitrate $AgNO_3$, a readily soluble colourless salt. Nitro-hydrochloric acid changes silver into insoluble chloride, AgCl.

Oxide of silver, Ag_2O, formed by precipitating a solution of a silver salt with one of caustic potash, is a brown or violet powder, slightly soluble in water (the solution has a feebly alkaline reaction), and easily soluble in ammonia. Oxide of silver, when heated to dull redness, readily breaks up into metal and oxygen. It neutralizes all acids, forming silver salts, of which the great majority are neutral and normal. There are very few acid or basic silver salts known.

3. **Reactions.**—Solutions of silver salts when mixed with *hydrochloric acid* give a white curdy precipitate of chloride, AgCl, absolutely insoluble in water and dilute acids generally, but slightly soluble in hydrochloric acid; easily soluble in ammonia, from which solution it can be reprecipitated by saturating the ammonia with an acid. All insoluble silver salts, except the iodide AgI and sulphide Ag_2S, are soluble in ammonia. *Sulphuretted hydrogen* precipitates black sulphide of silver, insoluble in water, in cold dilute acids, in ammonia, and in sulphide of ammonium. Sulphide of silver, when boiled with nitric acid, is changed into nitrate.

Silver salts, when heated on charcoal with *carbonate of soda*, yield a malleable bead of metal and no oxide-ring.

Lead.

4. **Lead** has a grey colour; is very soft, and nearly devoid of elasticity; specific gravity 11·4; melts at 330° C.; at a white heat it is slowly volatilized; in contact with air it is, at ordinary temperatures, slowly covered with a film of dark-coloured sub-oxide; when heated to redness in air it is pretty rapidly changed into oxide. Dilute nitric acid changes lead into nitrate, $Pb(NO_3)_2$, soluble in water, less so in nitric acid. Nitro-hydrochloric acid changes it into sparingly soluble chloride, $PbCl_2$.

5. **Oxide of lead** (litharge), PbO, is yellow; when heated it grows darker in colour; at a red heat it fuses.

Hydrate of lead, $Pb(HO)_2 = PbOH_2O$, formed by addition of caustic potash to a solution of a lead salt, is a white powder, which, when heated, loses water and is changed into oxide. It is easily dissolved by nitric and many other acids; also by potash.

Red oxide (minium), Pb_3O_4, is formed by keeping the yellow oxide in air at a dull red heat. At higher temperatures it is changed into oxygen and yellow oxide. Dilute nitric acid converts it into a solution of nitrate and insoluble peroxide, PbO_2.

6. **Peroxide of lead**, PbO_2, is a brown powder, insoluble in water, and in dilute acetic and nitric acids. Hydrochloric acid, especially in the heat, converts it into chloride, chlorine being liberated;—$PbO_2 + 4\,HCl = PbCl_2 + Cl_2 + 2\,H_2O$. When heated to redness it breaks up into oxygen and yellow oxide.

7. **Lead salts** are formed by the union of the oxide (PbO) with acids, with elimination of water. The solutions of the neutral salts do not change the colour of litmus paper. There is a great number of basic lead salts, mostly sparingly soluble in water. (Basic acetate is soluble, and has an alkaline reaction to test-papers.)

8. **Reactions of solutions of lead salts.**—*Sulphuretted hydrogen* precipitates black sulphide (PbS), insoluble in water and cold highly dilute acids, in sulphide of ammonium and in ammonia. Boiling hydrochloric acid converts sulphide of lead into chloride; hot nitric acid, into nitrate and sulphate (there is the more sulphate formed the stronger the acid). Boiling dilute (20°/₀) sulphuric acid converts it into sulphate, which remains undissolved. *Hydrochloric acid* precipitates chloride, $PbCl_2$, which is difficultly soluble in cold, easily in hot, water (a hot concentrated solution deposits, on cooling, crystals of chloride), little soluble in cold dilute acids, insoluble in ammonia. Hydrochloric acid is a

characteristic but not very sensitive reagent for lead. *Sulphuric acid* precipitates white sulphate, $PbSO_4$, nearly insoluble in water and still more insoluble in dilute sulphuric acid and in alcohol; readily soluble in hot hydrochloric and in hot nitric acid.

Dry-way test.—Lead-salts when heated on charcoal with *carbonate of soda* in the reducing flame, yield a malleable bead of metal and a yellow oxide-ring.

Mercury.

9. **Mercury** is the only metal which is liquid at ordinary temperatures; it solidifies at —39° C.; boils at 357° C., and is changed into a colourless vapour; specific gravity at 4° C. = 13·596. It has a silvery-white colour, and is not changed in air of ordinary temperature. At temperatures near its boiling point it slowly takes up oxygen from the air, and is partially converted into red oxide, HgO; at considerably higher or lower temperatures the metal is not affected. Nitric acid in the cold gradually converts it into difficultly soluble mercurous nitrate, which, by an excess of nitric acid and heating, is changed into easily soluble, non-crystallizable mercuric nitrate. Nitro-hydrochloric acid, on heating, changes it into the soluble chloride $HgCl_2$ (corrosive sublimate).

10. **Mercuric oxide**, HgO, is prepared by heating any mercury nitrate, when it remains as a crystalline mass, red in the cold, black in the heat. When strongly heated, it breaks up into metal and oxygen. Mercuric oxide can also be prepared by precipitating solutions of mercuric salts with caustic potash; thus prepared it is an orange-yellow powder. It is insoluble in water; it unites with acids to form mercuric salts.

11. **Mercurous oxide**, Hg_2O, formed by the action of caustic potash on mercurous chloride, is a black powder. In the light it gradually breaks up into metal and red oxide. It is insoluble in water; it combines with acids to form mercurous salts.

12. **Reactions of mercury-salts generally.**—All mercury-salts, *when heated, either volatilize* undecomposed (*ex.*:

the haloids $HgCl$, $HgCl_2$, HgI_2; the sulphide), or they are decomposed in such a way that mercury goes off as metal. In case of mercury-salts of non-volatile acids, the acid, or a decomposition product of it, remains (*e.g.* phosphate leaves phosphoric acid; chromate leaves chromic oxide). All mercury-salts, when mixed with *carbonate of soda* and heated in a bulb-tube, yield a sublimate of metallic mercury. In case of small quantities the sublimate forms a grey ring, which, when scraped together, unites into distinct globules. The smallest traces of such a mercury-sublimate may be identified by heating it gently in iodine vapour, when it will be converted into mercuric iodide, which is yellow at first but soon becomes red, especially when rubbed with a glass rod. *Acid solutions of mercury salts*, when treated with *metallic copper*, give a deposit, adhering to the copper, of metallic mercury, which either is silvery white or becomes so when gently rubbed with paper. The copper strips, after being washed and dried, when heated in a tube, yield a sublimate of metallic mercury; while the copper regains its natural colour. In this test the presence of nitric or other oxidizing acids should be avoided.

13. Reactions of solutions of mercurous salts.—(Salts of 'Mercurosum.')— *Hydrochloric acid* precipitates all the metal as mercurous chloride $HgCl$ (calomel); insoluble in dilute acids in the cold; soluble, through being changed into mercuric chloride, in nitro-hydrochloric acid; converted by ammonia into a black insoluble substance NH_3HgCl.

Sulphuretted hydrogen gives a black precipitate, which is a mixture of mercuric sulphide and metal. Hot nitric acid extracts from this precipitate the metal and leaves the sulphide.

Ammonia gives a black precipitate of varying composition.

14. Reactions of solutions of mercuric salts.—(Salts of 'Mercuricum.')—*Hydrochloric acid* gives no precipitate.

Sulphuretted hydrogen, when gradually added, gives first a white precipitate, which, on further addition of the reagent becomes yellow, orange, and at last, when there is an excess of reagent, black. The precipitate, then, is sulphide, which is insoluble in water, in cold dilute acids, in sulphide of ammonium, and in boiling nitric acid. Nitro-hydrochloric acid converts it into soluble mercuric chloride, $HgCl_2$. *Ammonia*, when mixed with a solution of mercuric chloride, gives 'white precipitate,' $NH_2Hg''Cl$.

Copper.

15. **Pure metallic copper** has a pale red colour; it is extremely tenacious and ductile; specific gravity=8·9. It is difficultly fusible (at ab. 1400° C.), and not at all volatile, on charcoal before the blowpipe. Copper remains unaltered in dry air; in moist air it is slowly covered with a green film of carbonate. When heated in air to dull redness it is changed, first into red cuprous oxide Cu_2O, then into black cupric oxide CuO. If copper is fused in presence of air the suboxide formed unites with the metal; hence most samples of commercial copper contain a little oxygen. The physical properties of copper are profoundly modified by even small admixtures of certain foreign elements. Nitric acid easily dissolves copper: the solution contains nitrate $Cu(NO_3)_2$. Nitro-hydrochloric acid changes it into soluble chloride, $CuCl_2$.

16. **Cupric oxide**, prepared by heating copper in oxygen, or heating the nitrate, is a black solid, infusible at a bright red heat. When heated in a current of hydrogen, or carbonic oxide, it is easily reduced to metal. Cupric oxide is insoluble in water; dilute acids dissolve it forming cupric salts. Most cupric salts have a blue or green colour.

17. **Reactions of solutions of cupric salts.**— *Hydrochloric acid* gives no precipitate. *Sulphuretted hydrogen* precipitates black sulphide, CuS; insoluble in water and in cold dilute acids generally; insoluble in boiling dilute sulphuric, and scarcely attacked by boiling (20°/₀) hydrochloric acid; very little soluble in *sulphide of ammonium;* soluble, as nitrate, in hot nitric acid; and, as chloride, in nitro-hydrochloric acid. *Ammonia* gives a pale

blue precipitate of basic salt, soluble in excess of ammonia, forming a deep blue solution. *Ferrocyanide of potassium* gives a brown precipitate, insoluble in HCl. This test is extremely delicate. *Metallic iron*, from slightly acid (and metallic zinc from acid or alkaline) solutions, precipitates metallic copper. If the reaction is performed in a platinum basin, the copper forms a coating on the platinum, so that it is accessible to further examination. *Dry-way tests.*—Copper-compounds when heated with *carbonate of soda* on charcoal in a reducing flame, yield metallic copper, in the shape of small scales disseminated throughout the flux; there is no oxide-ring formed. When fused with *borax* in the oxidizing flame, they yield a transparent green glass, which, when exposed to the reducing flame, becomes brown-red and opaque. The reduction succeeds more easily on addition of a trace of binoxide of tin.

18. **Cuprous salts.**—A solution of cupric chloride in hydrochloric acid, when treated with metallic copper, air being excluded, becomes first coffee-brown and at last colourless. The liquid then contains all the metal as cuprous chloride, CuCl, which, on addition of much water, is precipitated as a white powder. An ammoniacal solution of a cupric salt is, by prolonged contact with metallic copper, decolourized and changed into one of cuprous salt. Solutions of cuprous salts are colourless; when exposed to the air they eagerly absorb oxygen, with formation of cupric salt.

Bismuth.

19. **Bismuth** is reddish-white, of a crystalline structure, and so brittle that it can easily be powdered in a mortar; specific gravity=9·8. It fuses at 264° C., and can by a strong heat be volatilized. At ordinary temperatures it is not changed by contact with air; when heated in an oxidizing flame it burns with a blue flame and forms yellow oxide, Bi_2O_3. Nitric acid easily dissolves it; the liquid contains bismuth nitrate, $Bi(NO_3)_3$ dissolved in nitric acid. Nitrohydrochloric acid converts it into the chloride, $BiCl_3$.

20. **Bismuth oxide**, Bi_2O_3, as produced by burning the

metal or igniting the nitrate or hydrate, is a yellow powder, which, on heating, deepens in colour, and can be fused at higher temperatures. When heated in hydrogen it is reduced to metal. It is insoluble in water.

Bismuth hydrate, $Bi(HO)_3$, prepared by precipitating a solution of a bismuth-salt with ammonia, is a white powder insoluble in water, insoluble also in aqueous alkalies and in ammonia; when boiled with caustic potash it becomes yellow. The oxide and hydrate combine with acids to form 'bismuth salts.'

21. Reactions of bismuth-salts.— All normal bismuth-salts when treated with water are either not dissolved at all or are decomposed into an insoluble basic salt, and a solution of free acid holding a part of the oxide in solution. The basic salts produced by small quantities of water can be dissolved in nitric or hydrochloric acid, but if the quantity of acid added was not too large, the solutions are again precipitated when largely diluted with water. The reaction succeeds best with the chloride. Bismuth chloride, or a solution of the same in (*not too much*) hydrochloric acid when largely diluted with water, is decomposed into insoluble basic chloride, containing the *whole* of the metal, and into hydrochloric acid. (The precipitate is *not* dissolved by a solution of tartaric acid; the precipitate got by treating antimony trichloride, $SbCl_3$, with water *is* dissolved by tartaric acid solution.) A solution of a bismuth-salt in dilute acid behaves to reagents as follows:—*Sulphuretted hydrogen* precipitates black sulphide, Bi_2S_3; insoluble in cold dilute acids and in sulphide of ammonium; easily dissolved, as nitrate, by hot nitric acid; and, as $BiCl_3$, by hot hydrochloric acid, scarcely attacked by boiling 20°/₀ sulphuric acid. *Ammonia* precipitates white hydrate, insoluble in excess of the reagent. *Iodide of potassium* precipitates, from nitrate, brown of $Bi\,I_3$ soluble in excess of the iodide. [A neutral or slightly acid solution of nitrate of *lead*, when mixed with iodide of potassium, gives a *lemon-yellow* precipitate (PbI_2), which on boiling dissolves, and, if the liquid be then allowed to cool, crystallizes out again in beautiful yellow laminæ. The slightest admixture of bismuth salt discolours these crystals in the direction of orange or brown. (Abel and Bloxam.) *Dry-way test.*—A bismuth compound, when fused with sodium carbonate on charcoal in a reducing flame, yield a *brittle* bead of bismuth and a yellow oxide-ring.

Cadmium.

23. **Cadmium** is white, somewhat soft, and ductile; it fuses at 320° and boils at 860.° It is not changed by contact with dry air at ordinary temperatures; when strongly heated it burns, producing a brown smoke of oxide, CdO. Cadmium does not decompose water; strong hydrochloric and dilute sulphuric acids dissolve it slowly, with evolution of hydrogen. Nitric acid dissolves it, forming the nitrate, $Cd(NO_3)_2$, and ammonium nitrate; nitro-hydrochloric acid changes it into soluble chloride, $CdCl_2$.

24. **Cadmium oxide**, CdO, prepared by burning the metal or heating the nitrate, is a brown powder, infusible at a red heat, and non-volatile. When heated in a current of hydrogen or on charcoal it is reduced to metal.

25. **The hydrate**, $Cd(HO)_2$, prepared by precipitating the solution of a salt with caustic potash, forms a white powder, insoluble in water. The oxide and hydrate unite with acids and form salts.

26. **Reactions of Solutions of Cadmium-salts.**—

Sulphuretted hydrogen precipitates *yellow* * sulphide, CdS, insoluble in very dilute cold acids,—though not to the same extent as the other sulphides of this group; insoluble also in sulphide of ammonium, and in ammonia. Boiling dilute sulphuric acid, as well as hydrochloric acid, decomposes the sulphide, with evolution of sulphuretted hydrogen and formation of soluble salts. *Ammonia* gives a white precipitate of hydrate, soluble in excess. *Dry-way test.*—Cadmium salts, when fused with *carbonate of soda* on charcoal in a reducing flame, are reduced to metal, which is completely volatilized, and, on passing through the oxidizing portion of the flame, changed into oxide, part of which is deposited on the charcoal as a brown ring.

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* All the other sulphides of the group are dark-brown or black.

Summary and Additions.

27. The **metals** of the *copper group* are without action at any temperature on water or steam, and (with exception of *caamium*, which is slowly dissolved with evolution of hydrogen) are not attacked, in absence of air, by even boiling *dilute sulphuric* or *hydrochloric acid.* *Concentrated sulphuric acid*, in the heat, converts them into sulphates according to the general equation: $Me + 2H_2SO_4 = Me''SO_4 + SO_2 + 2H_2O$. They are all dissolved, as nitrates, by nitric, and, as chlorides, by nitro-hydrochloric acid.

28. The **oxides** of the group, when heated to redness in an atmosphere of *hydrogen* or *carbonic oxide*, those of silver or mercury when heated even in oxygen, are reduced to metal.

29. From the solutions of their chlorides or sulphates, the metals are all completely precipitated, as such, by *metallic zinc.*

30. From the neutral, alkaline or sufficiently dilute acid solutions of their **salts**, the metals of the copper group are completely precipitated, as sulphides, by *sulphuretted hydrogen;* the sulphides are insoluble in water and in highly dilute acids, insoluble also in ammonia, in carbonate of ammonia and in sulphide of ammonium.* By these reactions the *group* can be distinguished, and separated, from all other metals.

31. Supposing the metals of the copper group (or their oxides) to be severally treated with hot **nitric acid**, they all dissolve, the mercury—in general—as a mixture of mercurous nitrate, $Hg_2ON_2O_5$ and mercuric nitrate, $HgON_2O_5$; the bismuth as $Bi(NO_3)_3$ the silver as $AgNO_3$, the rest as $Me''(NO_3)_2$; † of these nitrate solutions, those of silver and lead only can be evaporated to *dryness* without fear of decomposition, but they can all, by cautious evaporation at a gentle heat, be converted into very concentrated solutions of the nitrates in nitric acid.

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* Comp. § 17.

† Comp. § 23.

32. Supposing these residues to be severally treated with **much water**, then—

The *silver*, *lead*, *cadmium*, and *copper salts* simply dissolve; while

The *mercury* and the *bismuth* salts are decomposed, with formation of *insoluble* basic nitrate, which, in each case, can be re-dissolved by nitric acid. On addition to the turbid liquids of *chloride of sodium*,

The *mercurous* salt is completely converted into insoluble chloride, HgCl,

The *bismuth* salt (partially at least) into insoluble oxychloride, and

The *mercuric* salt dissolved, with formation of $HgCl_2$.

33. Solutions of the several *nitrates* in water, or dilute nitric acid, when mixed with **hydrochloric acid**, behave as follows:

The *silver* is completely precipitated as chloride, insoluble in acids, soluble in ammonia; from the ammonia solution the chloride can be reprecipitated by means of nitric acid;

The *mercurosum* is completely precipitated as calomel, HgCl, which is insoluble in cold dilute acids, but by the action of *ammonia* converted into a *black* insoluble substance.

The lead (from sufficiently strong solutions) is *partially* precipitated as chloride $PbCl_2$, which is easily soluble in boiling water, but *not* dissolved (or discoloured) by ammonia;

The *bismuth*, from strong solutions containing little free acid, *may* be partially precipitated as oxychloride.

No other metallic nitrates (except *thallious*) yield precipitates of chlorides on addition of hydrochloric acid.

34. Metallic nitrates generally, when repeatedly *evaporated* with strong *hydrochloric acid*, are (substantially at least) converted into chlorides.

35. Supposing this operation to have been applied to the nitrates of those metals of the copper group which are not completely precipitated by hydrochloric acid, and the chloride solutions to have been concentrated by evaporaation, as far as possible, without decomposing the chlorides,* the residues will consist of (aqueous hydrochloric acid and) $BiCl_3$, $PbCl_2$, $HgCl_2$, $CuCl_2$, $CdCl_2$, respectively.

Supposing these to be treated with **much water**, then

The *bismuth* is completely precipitated as basic chloride; while

All the *other chlorides* simply dissolve.

36. If the resulting (clear or turbid) solutions are saturated with *sulphuretted hydrogen*, the metals are completely precipitated as sulphides.

The behaviour of these **sulphides** to hot **dilute mineral acids** is as follows :—

	Dissolves	Leaves undissolved
Boiling 20% **Sulphuric Acid.**	CdS as $CdSO_4$.	Bi_2S_3†, CuS, HgS, as such; PbS as $PbSO_4$.
Boiling 20% **Hydrochloric Acid.**	CdS, Bi_2S_3, PbS as chlorides ($PbSO_4$ as such).	CuS,† HgS.
Boiling (pure) **Nitric Acid** of 1·2 sp. gr.	All, except HgS, as nitrates.	HgS.
Boiling **Aqua Regia**, or Hydrochloric Acid on addition of Chlorate of Potash.	All as chlorides.	None.

NOTE.—Sulphate of lead, from its solution in hydrochloric acid, is reprecipitated on moderate dilution with water.

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* Remember that chloride of bismuth, although non-volatile from its acid solution, is volatilized when heated by itself.

† Slightly attacked.

37. **Lead** and **Mercurosum** are the only metals of the *copper group** which from acid solutions of their salts are precipitated by *sulphuric acid.*

38. Behaviour of *ammonia* to solutions of

Lead, **Bismuth,** **Mercuricum,**	White precipitate, insoluble in excess of ammonia.
Mercurosum,	Black precipitate, insoluble in excess of ammonia.
Silver, **Cadmium,**	Precipitate, soluble in excess of ammonia, giving a colourless liquid.
Copper,	Pale blue precipitate, soluble in excess of ammonia, giving a dark *blue* liquid.

From the above data (and what was said in Exercise XXXII.) we see our way to more than one method for the

39. *Exhaustive Examination of a solution of Salts for* **Metals** *of the* **Copper group.**

To students who have not yet got far enough advanced to invent their own methods, we recommend the following process, in the explanation of which, to avoid circumlocution, we will suppose all the metals of the group to be present, say as nitrates.

Begin by adding to the solution *hydrochloric acid*, drop by drop, shaking up violently after each addition, until the precipitate no longer increases, wash the precipitate by decantation with cold water, and filter the decanted liquids. How the precipitate can be examined for lead, silver, and mercurosum follows at once from what was stated in §§ 33, 37.

To separate out of the *filtrate* (from the chlorides) what is left of the group, first of all test for *nitric* and other oxidizing acids by adding to a portion of the liquid one drop of indigo solution and heating: if the indigo is decolourized —which indicates the presence of the class of acids named —evaporate the filtrate to a small volume, add some fuming hydrochloric acid, evaporate again, and after having thus converted the metals into chlorides, dilute with water and precipitate completely with *sulphuretted hydrogen*. This is best done in a flask, and the precipitation may be looked upon as completed, if the liquid, after having been violently shaken, smells strongly of the gas, and a filtered portion, when largely diluted with sulphuretted hydrogen water, undergoes no visible change. Wash the precipitate, first two or three times with cold very dilute sulphuretted hydrogen water, and then completely with hot water. To extract the metals of the arsenic group, digest the precipitate with yellow sulphide of ammonium, in a flask, filter off what is left, and wash again. The precipitate now consists (potentially) of the sulphides HgS, PbS, Bi_2S_3, CuS, CdS. To separate these metals, mix the precipitate with 20°/₀ *hydrochloric acid*, pass through the mixture some bells of sulphuretted hydrogen (to resulphurize any copper that may, by the action of the air, have passed into solution), boil for some minutes, dilute, filter, and wash with hot water. The cadmium, lead, bismuth, and a trace of the copper pass into the filtrate (**F**), while the *mercuricum* and the bulk of the *copper* remain in the residue (**R**).

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* A precipitate formed in a complex solution of salts may contain, besides the two metals named, also barium, strontium, and possibly calcium.

From **F** eliminate the *bismuth* by evaporating to a small bulk and diluting with much hot water. To the filtrate add a few drops of sulphuric acid, evaporate to a very small bulk, and then dilute again moderately with water: the *lead* will be precipitated as sulphate. From the filtrate precipitate the *cadmium* (and copper) with *sulphuretted hydrogen*, and, if necessary, separate the washed sulphides by means of boiling 20°/₀ sulphuric acid: the cadmium dissolves and can be reprecipitated from the solution by sulphuretted hydrogen. The residual sulphide of copper can be dissolved by means of hot hydrochloric acid and a granule of chlorate of potash, and be identified by means of ferrocyanide of potassium.

To examine **R**, dissolve it in hot hydrochloric acid, with the help of some chlorate of potash. In the solution the mercuricum and copper can be recognised side by side of each other, the former in one portion by means of metallic copper or stannous chloride (which, in solutions of $HgCl_2$ produces a precipitate of HgCl); the copper in another by means of ammonia (comp. §§ 12, 17). To *separate* the two metals, heat the solution with *phosphorous acid* to 60° C., the mercury is, after some time, completely precipitated as calomel; the copper remains dissolved.

APPENDIX.

40. Palladium is a rare metal; a constant constituent of platinum ore, but scarcely occurring anywhere else. The compact metal is intermediate in lustre and colour between silver and platinum. It is just barely fusible in a forge fire, but easily in an oxyhydrogen flame; the molten metal absorbs oxygen and 'spits' like silver. Specific gravity of the hammered metal = 12 (about). The metal when exposed to an atmosphere of hydrogen, or—what is better—when used as the negative electrode in the galvanic decomposition of acidulated water, absorbs up to 0·54% of its weight of hydrogen, suffering at the same time a considerable expansion. The absorbed gas can be expelled by continued application of a red heat in a vacuum; the residue differs from normal palladium, being spongy and comparatively brittle. Palladium is scarcely attacked by even hot sulphuric or hydrochloric acid; nitric acid dissolves it slowly without gas-evolution; aqua regia dissolves it very readily. The solutions are brown, and contain $Pd(NO_3)_2$ and $PdCl_2$ respectively.

41. From either the metal is precipitated as such, by phosphorus, sulphurous acid, copper and other reducing agents. *Sulphuretted hydrogen* gives a black precipitate of sulphide, insoluble in sulphide of ammonium. *Iodide of potassium* or hydriodic acid gives a black precipitate of iodide, visible even in liquids diluted to 500,000 times the weight of the metal. *Cyanide of mercury* precipitates white cyanide $PdCy_2$. *The chloride* forms double salts with the chlorides of the alkali-metals, composed according to $PdCl_2R_2Cl_2$, and all soluble in water. A concentrated solution of the chloride $PdCl_2$

when treated at a gentle heat with chlorine or aqua regia, becomes almost black, and, on addition of chloride of potassium, now gives a crimson precipitate of the composition $PdCl_4 2KCl$, which is far more stable than the chloride $PdCl_4$ from which it originated.

B. ARSENIC GROUP.

ARSENIC, ANTIMONY, TIN (MOLYBDENUM, TUNGSTEN). GOLD, PLATINUM (PLATINUM METALS, EXCEPT PALLADIUM).

Arsenic.

42. The metal '**Arsenicum**' possesses a crystalline structure, and is very brittle. When pure it is steel-grey; but in contact with air soon gets covered with a dark-coloured dull coating of a sub-oxide, which, when boiled with water, breaks up into metal and a solution of the trioxide, As_2O_3. Specific gravity = 5·96. When heated in a sublimation-tube, the metal, at a temperature below dull redness, volatilizes without first melting; the vapours condense in the upper part of the tube into a 'mirror.' When heated in a large test-tube or in a draught-tube (*i.e.* with much air) it is readily oxidized into vapour of trioxide As_2O_3 which, in the colder parts, condenses, forming colourless, transparent, sparkling crystals. Dilute *hydrochloric* or *sulphuric acid* does not act much on (pure) arsenicum; concentrated sulphuric acid converts it into As_2O_3, sulphurous acid being evolved. *Nitric acid* changes it, first, into the trioxide, and then into arsenic acid H_3AsO_4.

43. The **Trioxide** As_2O_3 ('white arsenic'), if recently prepared on a large scale by sublimation, forms colourless, translucent, amorphous cakes, very tough and difficult to break, which, after some time, become crystalline, opaque (porcelain-like), and brittle. It is in the latter shape that

the oxide usually occurs in commerce. The amorphous variety dissolves in 50 parts of cold and in 10 parts of boiling water; the crystalline variety is less soluble. It is easily soluble in hydrochloric acid; the solution contains, in general, $AsCl_3$ beside As_2O_3; the former predominating the more the stronger the acid. . On distillation the *chloride* passes over, with the last fractions of the menstruum. By the action in the heat of strong nitric acid, or of aqua regia, or of hydrochloric acid and chlorate of potash, the trioxide is readily oxidized into arsenic acid. The oxide easily dissolves in aqueous caustic potash or soda, and in aqueous alkaline carbonates, being converted into *arsenite.* Arsenious oxide vapour, when passed over red-hot *charcoal*, is reduced to metal. By this reaction the least fragment of the oxide may be identified with perfect certainty. (Compare Exercise V.)

44. Arsenic acid H_3AsO_4, forms colourless crystals, easily soluble in water. When heated by itself it is dehydrated, and thus reduced to **pentoxide** As_2O_5, a white mass which at an incipient red heat fuses, and at a higher temperature breaks up into trioxide and oxygen. Arsenic acid is *tribasic*, but $2KHO$ or $2NaHO$ (for $1H_3AsO_4$) suffices to neutralize its action on litmus.

Reactions of solutions of Arsenious and Arsenic Acids.

45. Arsenious solutions.—An aqueous solution of the 'acid' (*i.e.* a solution of As_2O_3 in water), when mixed with *sulphuretted hydrogen*, assumes a yellow colour; on addition of hydrochloric acid a yellow precipitate of the sulphide, As_2S_3, is formed, which, if there be enough of the reagent, contains the whole of the metal. Solutions of arsenites, when acidified with hydrochloric acid, behave in the same way. The *sulphide* precipitate does not oxidize in contact with air; it is very slightly soluble in sulphuretted hydrogen water, easily soluble in solutions of *sulphide of ammonium*, and in those of the carbonates of, or of caustic, ammonia.

From these solutions it is reprecipitated on the alkalies being saturated by hydrochloric acid. Arsenic tersulphide is scarcely attacked, at ordinary temperatures or at a gentle heat, by even fuming hydrochloric acid. When heated with aqua regia, or hydrochloric acid and chlorate of potash, it is dissolved as *arsenic acid.* From neutral solutions of alkali-arsenites, *nitrate of silver* precipitates a yellow silver salt of the composition As_2O_3, $2Ag_2O$, which is soluble in nitric acid, in ammonia, and in large quantities of nitrate of ammonia. To obtain the precipitate from a solution of the teroxide in water, or in very dilute nitric acid, add nitrate of silver, and then, by means of a glass rod, drop by drop, enough of highly dilute ammonia to saturate the acids, but no more. *Metallic copper*, from hydrochloric solutions of the trioxide, precipitates the metal in the shape of a steel-grey deposit on the copper, consisting of an alloy of the two metals. If the arseniuretted copper be heated in a draught-tube, a part of the arsenicum is volatilized as, and obtained as a sublimate of, white arsenic. This test, *Reinsch's*, is very sensitive.

46. Arsenic (As_2O_5) solutions.—An aqueous solution of the acid, when treated with *sulphuretted hydrogen*, remains at first apparently unchanged, even in presence of hydrochloric acid; but after some time a precipitate is gradually formed. A complete precipitation requires about twenty-four hours. At 60°-70° C., however, and in presence of hydrochloric acid, the precipitation begins immediately, and is soon completed. The yellow precipitate is a *mixture* of the composition $As_2S_3 + S_2$. The precipitate obtained on acidifying an alkaline solution of arseniate, which has previously been saturated with sulphuretted hydrogen, and thus converted into thi-arseniate, *is* As_2S_5. The compound As_2S_5 exhibits pretty much the same solubility relations as the tersulphide. From solutions of *alkali-arseniate*, '*magnesia-mixture*'* precipitates the acid, gradually, as a white crystalline double salt of the composition $AsO_4Mg''NH_4 + 6H_2O$, which is slightly soluble in water, and in solutions of ammonia salts, but almost insoluble in dilute ammonia.[*] *Arsenites*, under the same circumstances, are not precipitated.

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* A mixture of chloride of magnesium, chloride of ammonium, and excess of ammonia.

47. A solution of **either oxide of arsenic** in *fuming* hydrochloric acid, when mixed with one of *stannous chloride* in the same menstruum, gives a brown precipitate, consisting substantially of metallic arsenic, but always yielding on calcination from 1 to 5% of stannic oxide. If the mixture contains enough of real hydrochloric acid to emit copious fumes, the whole of the arsenic is precipitated; in more dilute liquids, a part, at least, of the arsenic remains dissolved, or there may be no precipitate at all. Solutions of antimony-oxides in hydrochloric acid do not exhibit this reaction. The test indicates 1 part of arsenic in 400,000 parts of mixture.—(*Bettendorf.*)

48. **Arseniuretted hydrogen**, AsH_3.—When a solution of any arsenic *oxide* in water or acid is treated with *metallic zinc* and hydrochloric or dilute sulphuric acid (with 'nascent hydrogen'), a part of the arsenic is precipitated as metal, while the rest escapes with the excess of hydrogen as gaseous hydride AsH_3. If the mixed gas be passed through a red-hot glass tube, the hydride undergoes at least partial dissociation, the metal being deposited at some distance from the heated portion of the tube in the form of a dark grey resplendent '*mirror*.' The mixed gas burns with a bluish white flame (a pure hydrogen flame is barely visible), and deposits on a porcelain plate held in it metallic-looking '*stains*' of arsenicum. By this (*Marsh's*) test the least trace of arsenic oxide or chloride can be detected. The *modus operandi* is as follows:—

49. Into a gas-evolution bottle of about 500–700 c.c. cap-

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[*] From orthophosphoric acid, which behaves to magnesia salt, etc., in a precisely analogous way, arsenic acid is easily distinguished by means of sulphuretted hydrogen, which does not act on H_3PO_4.

acity—which must be provided with a funnel-tube for adding liquid without lifting the stopper, and the exit-tube of which should be connected, through a cotton-wool tube, with a long *hard* glass tube about 5 mm. wide inside, and drawn out to a fine point at the end—place about 50 grammes of *granulated zinc*, and then (through the funnel) add enough of 10°/₀ sulphuric[*] or 10°/₀ hydrochloric acid to produce a moderate evolution of hydrogen, which must be maintained by occasional addition of fresh acid. Wait until the gas within the apparatus is no longer explosive, *i.e.* until a small quantity of it, collected over water in a test-tube, on being kindled, burns quietly, the flame travelling slowly down towards the bottom of the tube. Now light the gas issuing from the drawn-out tube, heat a portion of the same tube to redness with a Bunsen's lamp, and in order to make sure of the purity of the reagents, allow the process to go on *au blanc* for at least ten minutes. If no deposit is formed in the tube after that time, wait first until the gas-evolution has become very slow, because if now the solution to be tested is poured in, the reaction at once increases in energy, sometimes to such an extent that it is necessary to moderate it by plunging the gas-evolution bottle into cold water. If the liquid added contains, however little, arsenic, a mirror will sooner or later appear in the heated tube, and the flame will yield stains on porcelain. If no indication of arsenic is obtained within, say, a quarter of an hour, this element may be assumed to be absent. Very minute quantities of arsenic may give only a mirror, but no stains. *Arseniuretted hydrogen*, when passed through a solution of *nitrate of silver*, is, at least partially, absorbed and decomposed according to the equation: $2AsH_3 + 6Ag_2ON_2O_5 + 3H_2O = 6Ag_2 + 6N_2O_5H_2O + As_2O_3$. The filtered liquid therefore, when *cautiously* saturated with ammonia, and mixed, if necessary, with a drop more of nitrate of silver, will give a yellow precipitate of arsenite of silver. (Comp. § 45; and also § 57, under 'Antimony.')

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[*] A stronger acid would yield H_2S, which greatly interferes with the reaction.

50. Many metallic arsenides, arsenites, and arseniates, and other arsenic compounds, when heated on charcoal in a reducing blowpipe flame, lose a part at least of their arsenic as metal, which in passing through the flame is oxidized to trioxide. This process is always accompanied by an intense, characteristic *garlic-like smell*, owing not to the metal or oxide As_2O_3—but probably to a suboxide, or perhaps a trace of hydride, formed in the process.

Antimony.

51. Antimony is a greyish white metal of marked crystalline structure, very brittle, and easily powdered in a mortar. Spec. grav. = 6·82. It melts at 450°, and when heated further in a stagnant atmosphere, remains practically unvolatilized at even a bright red heat; in a current of hydrogen, however, it may be volatilized within a glass tube at temperatures producible by means of a Bunsen's lamp. But its volatilization at such temperatures can be completely stopped by covering it with a flux, such as cyanide of potassium or carbonate of soda and potash, etc. When heated on charcoal in an oxidizing blowpipe-flame it burns with a bluish flame and formation of a white smoke of oxide. When heated on charcoal in the reducing flame, it is gradually volatilized; the vapour in passing out of the flame burns into white oxide, of which a part is deposited on the charcoal as a white oxide ring. This deposit, when touched with an oxidizing flame, is readily volatilized, without any previous change of colour, which distinguishes it from oxide of zinc. When a globule of antimony is strongly heated on charcoal and then left to itself, it continues glowing for some time and emitting the white oxide smoke, and if a current of cold air be directed against it by means of the blowpipe it continues burning like a piece of charcoal. This experiment does not succeed if the metal is contaminated with iron or any other impurity causing the formation on the globule of an infusible coating. The vapours formed in the volatilization of *pure* antimony on charcoal by means of a reducing flame possess no smell, while the slightest admixture of *arsenic* will give rise to a perceptible garlic-like odour.

52. Antimony is scarcely attacked by even boiling 20°/₀ *hydrochloric* or dilute sulphuric acid. *Concentrated sulphuric acid* in the heat converts it into trioxide, Sb_2O_3. Hot *nitric acid* converts it into trioxide or pentoxide, Sb_2O_5, or a mixture of the two. Both oxides are insoluble in nitric acid, but are dissolved by a boiling solution of tartaric acid. Nitro-hydrochloric acid readily dissolves the metal as trichloride or pentachloride ($SbCl_3$ or $SbCl_5$).

53. **The tri-oxide Sb_2O_3** when obtained in the dry way consists of white crystals. When heated in absence of air it fuses below a red heat, and then volatilizes ; in presence of air it is changed into the infusible and non-volatile amorphous oxide Sb_2O_4. It is easily soluble in hydrochloric and in tartaric acid, also in caustic potash.

54. **The terchloride $SbCl_3$**, prepared by distilling antimony with corrosive sublimate ($Sb_2+3HgCl_2=3Hg+2SbCl_3$), or by decomposing antimony sulphide with boiling strong hydrochloric acid, and removing the water and excess of acid by evaporation, is a buttery translucent mass, which melts at 72° and boils at 200° without decomposition. Water decomposes it into hydrochloric acid and antimony oxychloride, a white crystalline precipitate, which can be redissolved by hydrochloric and by tartaric acid.

55. **The pentachloride $SbCl_5$**, prepared by passing dry chlorine over metallic antimony, is a colourless, very volatile liquid, which fumes in the air. Water decomposes it into hydrochloric acid and the hydrate $Sb_2O_5.4H_2O$.

56. **Reactions of a solution of antimony terchloride in hydrochloric acid.**—*Water* precipitates basic chloride, soluble in hydrochloric and in tartaric acid (basic bismuth chloride does not dissolve in tartaric acid). The precipitation is the more complete, the less the quantity of free acid and the greater the amount of water added. *Sulphuretted hydrogen*

precipitates the orange red sulphide ($Sb_2S_3+xH_2O$), insoluble in water and in highly dilute acids, soluble in *sulphide of ammonium* and in caustic potash, but almost insoluble in a solution of *sesquicarbonate of ammonia.* Fuming hydrochloric acid, even in the cold, readily dissolves it as terchloride. From its solutions in the alkaline liquids named, the sulphide can be reprecipitated by acids. The hydrated sulphide, when heated to 200°, loses all its water and leaves anhydrous amorphous sulphide which at a higher temperature melts, and when subsequently allowed to cool gradually, is transformed into a black *crystalline* variety, identical with native sulphide (antimony-glance). *Metallic zinc* (also *iron*) precipitates metallic antimony as a black powder without metallic lustre. If the reaction is performed in a platinum vessel the antimony forms a dull black coating on the platinum; this reaction is very sensitive.

57. When a solution of antimony chloride or an acid solution of Sb-oxides generally, is added to a mixture of zinc and hydrochloric or dilute sulphuric acid, a part of the antimony is precipitated, while the rest is changed into gaseous antimoniuretted hydrogen SbH_3. The gaseous mixture when passed through a red-hot tube behaves like arseniuretted hydrogen, *i.e.* it deposits a mirror of metal. The gas burns with a white flame, which deposits on porcelain plates stains of metallic antimony. (Comp. § 49.) When passed through *nitrate of silver* the gas is decomposed in such a way that the whole of the antimony is precipitated as black $SbAg_3$.—$2SbH_3+3Ag_2ON_2O_5=2SbAg_3+6HNO_3$. To detect the antimony, wash the precipitate, and digest it with yellow sulphide of ammonium. The antimony dissolves as sulphide, which, on cautious evaporation of the filtrate, remains as a brick-red mass, readily decolourized by cold fuming hydrochloric acid. If arsenic be present, it can be detected as shown in § 49.

58. Antimonic acid $Sb_2O_55H_2O$ (*Fremy*), obtained by treating antimony with strong nitric acid, is a white powder sparingly soluble in water and in ammonia, slowly soluble in hydrochloric and in tartaric acid. When heated to redness, it is decomposed into oxygen, water and tetroxide.

59. **Meta-antimonic acid** $Sb_2O_5 4H_2O$, obtained by acting on antimonic pentachloride with water, is more readily soluble in ammonia than the preceding, and is soluble also in a large quantity of cold water. Solutions of the acid and of its salts on standing are changed into, respectively, antimonic acid and antimonates.

60. **Acid Potassium metantimonate** $K_2O,Sb_2O_5+7H_2O$, precipitates from solutions of sodium-salts, sodium metantimonate, almost insoluble in water, less soluble still in dilute alcohol.

61. An acid solution of either antimonic acid (or a solution of antimonate mixed with excess of mineral acid), when treated with *sulphuretted hydrogen*, gives an orange-red precipitate of Sb_2S_5, soluble in alkalies and alkaline sulphides, decomposed by boiling hydrochloric acid with formation of a solution of terchloride and separation of sulphur.

To zinc and hydrochloric acid antimonic solutions behave like antimonious.

62. To distinguish between Sb_2O_3 and Sb_2O_5 the following reactions may be used. A solution of Sb_2O_3 in alkalies gives with silver nitrate a black precipitate insoluble in ammonia; a solution of Sb_2O_5 gives a yellow precipitate soluble in ammonia. Sb_2O_5 when treated with potassium iodide and hydrochloric acid gives a brown solution containing free iodine; Sb_2O_3 gives a colourless liquid.

63. **Blowpipe Test.**—Non-volatile antimony compounds, when heated with carbonate of soda in the reducing flame on charcoal, give brittle globules of antimony, and an abundant white deposit of oxide; Sb_2O_3 and Sb_2O_4. (See §§ 51 and 53.)

Tin.

64. **Tin** has a white colour and a strong metallic lustre. It is very ductile, but slight admixtures of arsenic, antimony,

and some other metals greatly reduce its ductility. Pure tin in the form of ingot is of a crystalline and yet fibrous texture; when bent, it gives out a peculiar creaking sound, caused by the friction of the crystals against each other. Spec. grav. $= 7{\cdot}28$. It melts at 230° C., and is volatilized at a white heat. It does not tarnish in the air at ordinary temperatures, but when fused in air it gets covered with a film of oxide; at a stronger heat it burns into stannic oxide SnO_2. Tin is dissolved by hydrochloric acid, especially in the heat, with evolution of hydrogen and formation of stannous chloride $SnCl_2$; dilute sulphuric acid dissolves it slowly; hot concentrated sulphuric acid changes it into stannic sulphate; hot nitric acid converts it into metastannic acid, a white powder which does not dissolve in the acid. When heated in chlorine it is changed into stannic chloride $SnCl_4$. Nitro-hydrochloric acid converts it into a solution of the same chloride. Tin is also dissolved in the heat, with evolution of hydrogen, by caustic potash; the solution contains potassium stannate.

65. Stannous chloride crystallizes from its aqueous solutions in large transparent colourless prisms, of the composition $SnCl_2H_2O$. The aqueous solution, when kept in contact with air, absorbs oxygen and deposits a white precipitate of oxychloride Sn_2OCl_2, tetrachloride being formed at the same time.

66. Reactions of a solution of stannous chloride.—*Sulphuretted hydrogen* precipitates brown stannous sulphide, SnS, which is insoluble in water and in highly diluted cold acids; insoluble also in *colourless* sulphide of ammonium $(NH_4)_2S$. When treated with this reagent and sulphur, or with *yellow* sulphide of ammonium, it dissolves; the solution, when acidified, gives a *yellow* precipitate of stannic sulphide SnS_2. Stannous sulphide is soluble in caustic potash, and from the solution is reprecipitated, by acids, as SnS. Dilute hydrochloric acid on boiling—fuming acid at a gentle heat—converts the sulphide (SnS) into a solution of the dichloride $SnCl_2$. *Caustic potash* precipitates white hydrate $2SnO.H_2O$, soluble in excess of potash; the solution when boiled yields *metallic tin* and a solution containing *stannate* of potash; when evaporated slowly, it deposits black anhydrous stannous oxide, SnO. Stannous chloride, towards many substances, behaves as a powerful reducing agent. From solutions of mercuric chloride it precipitates calomel or metallic mercury; it reduces the (red) solution of chromic acid to (a green) one of chromic chloride; from a (green) concentrated solution of cupric chloride it precipitates (white) cuprous chloride, etc. etc. *Metallic zinc* precipitates grey resplendent crystals of metallic tin. (Metallic iron does *not.*) If the reaction is performed in a platinum dish, the metal is partially deposited on the platinum, as a grey coating, which, in presence of the least trace of *antimony*, assumes a *black* colour. Regarding the action of *terchloride of gold* see § 73.

67. The **tetrachloride** $SnCl_4$ is a colourless oil of 2·2 specific gravity, which, in contact with moist air, emits copious fumes. It boils at 112°. It acts violently on water, a small quantity of which converts it into crystals of $SnCl_4 3H_2O$, which readily dissolve in more water.

68. The solution behaves to **reagents** as follows:—*Sulphuretted hydrogen* gives a *yellow* precipitate of the sulphide SnS_2, which is insoluble in water and highly diluted acids, but soluble in caustic potash and in sulphide of ammonium, from which solutions it can be reprecipitated by acids. Stannic sulphide, while being washed with pure water, shows a great tendency to run through the filter; this can be prevented by addition to the wash-water of common salt or of acetate of ammonia. The recently precipitated sulphide is readily decomposed and dissolved, as $SnCl_4$, by tepid *fuming hydrochloric acid;* dilute acid acts similarly on boiling; hot *nitric acid* changes it into a precipitate of dioxide. It is slightly soluble in a solution of *sesquicarbonate of ammonia.* *Caustic potash* (also soda) gives a white precipi-

tate of hydrated dioxide, soluble in excess of the alkali. *Ammonia* precipitates the same hydrate which, by an excess of *this* reagent, is only slightly dissolved. The precipitation is *prevented* by the presence of *tartaric acid.* From solutions which do not contain too much free acid, certain alkali-salts, for instance *nitrate of ammonia* and *sulphate of soda*, precipitate the whole of the tin as hydrated dioxide. *Zinc*, in presence of some free acid, precipitates the tin as such. A solution of *hydrated dioxide** ('stannic acid') in hydrochloric acid behaves to reagents like one of the tetrachloride in water.

69. Metastannic acid, x($SnO_2 2H_2O$) (x being probably =5), is formed by the action of nitric acid on tin as a white powder, insoluble in *nitric acid. Hydrochloric acid* does not dissolve it immediately, but if the mixture be boiled for some time and then diluted with water, a clear solution is produced. This solution differs from one of *tetrachloride* in water (or hydrochloric acid) in some of its reactions. To *sulphuretted hydrogen*, *sulphide of ammonium*, *potash*, *nitrate of ammonia*, *sulphate of soda*, *zinc*, it behaves substantially—phenomenally at least—like one of tetrachloride. It differs from the latter in the following points :—*Sulphuric acid* readily precipitates even a concentrated solution of the *meta-acid*, while it precipitates that of the *tetrachloride* only if it is very dilute. *Carbonate of potash* (from the meta-solution) precipitates a bulky hydrate, *insoluble* in excess of reagent, while the corresponding precipitate from the tetrachloride dissolves in carbonate of potash. *Tartaric acid* does *not* prevent the precipitation of the meta-acid by *excess of ammonia.*

70. The stannic oxide, obtained by burning tin in air, and the native oxide (tinstone), are practically insoluble in acids. When fused with caustic potash in a silver crucible they are changed into potassium stannate, which is soluble in water.

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* *i.e.* of the substance precipitated from a solution of $SnCl_4$ by alkalies.

They can be rendered soluble also by fusion with three parts of carbonate of soda and three of sulphur, when they are converted into soluble thiostannate of sodium.

71. Dry-way tests.—Non-volatile tin compounds when fused on charcoal with carbonate of soda in a reducing flame yield *ductile* metallic tin, and no oxide ring. When a little cupric oxide is dissolved in a borax bead in the flame of a Bunsen's lamp, the bead is green, whether the oxidizing or reducing part of the flame be used; if now the least trace of stannic oxide be added, and the bead heated in the reducing part of the flame, it becomes dark red, the cupric oxide being reduced to cuprous oxide. In this experiment a blowpipe flame must not be used, as in it the reduction may be effected without the addition of tin. Oxide of tin when moistened with *cobalt solution* and heated on charcoal, in the oxidizing flame, assumes a *bluish* green colour. (Comp. § 188.)

Gold.

72. Gold has a peculiar yellow colour and great metallic lustre. It is very soft, and is the most ductile of metals. Spec. grav. = 19·3. It is somewhat more difficultly fusible than copper, and volatile only at the very highest temperatures. Before the blowpipe on charcoal it can be fused, but not at all volatilized. Gold is not attacked by oxygen, nor does it absorb it at any temperature. It is insoluble at any temperature, in any one *pure* mineral acid, whether strong or dilute. *Nitric acid*, holding lower nitrogen oxides in solution, attacks it perceptibly, but very slowly. *A mixture of nitric and hydrochloric acids** readily dissolves it as *terchloride* $AuCl_3$, which, by repeated evaporation of the solution at a gentle heat, first with fuming hydrochloric acid for the removal of the excess of nitric acid, and then with water for eliminating the hydrochloric acid, can be obtained pure. Alloys of gold with ordinary metals, the richness of which in gold exceeds certain limits, are not attacked by acids which would dissolve these metals when given for themselves. Thus, for instance, British standard gold (an alloy of 1 part of copper with 11 parts of gold) is not attacked by nitric acid. Gold is not attacked by fused *caustic potash or soda*, but fused *polysulphide* of potassium dissolves it, with formation of a double sulphide soluble in water. Finely divided gold dissolves also in an aqueous solution of sulphur in sulphide of potassium.

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* 'Aqua regia,' so called on account of its power of dissolving the king of metals.

73. Reactions of an aqueous solution of the terchloride $AuCl_3$.—*Sulphuretted hydrogen* produces a brown precipitate of sulphide Au_2S_3, little soluble in colourless, easily in yellow, sulphide of ammonium; from the solution the sulphide is reprecipitated on acidification. *Ferrous sulphate* precipitates metallic gold as a brown, sometimes as a purple, powder. Many other reducing agents, *e.g.* terchloride of arsenic, sulphurous acid, formic acid; also most metals (*e.g.* copper, mercury, zinc) precipitate gold, as such, from the solution of its chloride; at least they do so in absence of nitric acid. *Stannous chloride*, containing some tetrachloride, produces a purple colouration, and generally also an intensely coloured precipitate, of 'gold purple' (purple of Cassius). The shade of colour depends on the relative quantities of the substances acting upon one another. The precipitate contains gold, tin, and oxygen; its constitution is not known.

74. Most gold compounds leave on ignition a residue containing, or consisting of, metallic gold. The terchloride, when exposed to the temperature of melting tin, is reduced to aurous chloride AuCl, a white saline mass, which, by the action of water—slowly in the cold, but rapidly on boiling—is decomposed into metal and terchloride.

Platinum.

75. Platinum is a metal of a light steel-grey colour, very ductile, though not to the same degree as gold or silver. Spec. grav. =21·5. Platinum is perfectly infusible at temperatures producible by the blowpipe or an ordinary furnace; by means of the oxyhydrogen flame it can be fused. It remains perfectly unaltered in air at any temperature. It is not attacked by hydrochloric or pure nitric acid, nor even by boiling concentrated sulphuric acid; aqua regia, in the heat, dissolves it, forming the tetrachloride $PtCl_4$. When alloyed with silver it *may* be dissolved by pure nitric acid. The hydrates and sulphides of potassium and sodium, when in the state of fusion, attack platinum strongly; it is also attacked, but less strongly, by fused caustic baryta. Phosphorus, also arsenic, and many metals, such as lead, tin, antimony, etc., when heated with platinum, unite with it, forming easily fusible alloys.

76. The tetrachloride $PtCl_4$ is a dark brown substance, easily soluble in water, forming an intensely brownish-red solution; very dilute solutions show a yellow colour. When the chloride is heated to about 300° C. it loses chlorine and is changed into the dichloride $PtCl_2$, a brown or greenish-grey powder insoluble in water, but soluble in hydrochloric acid, and in a solution of the tetrachloride, imparting to the latter a very dark colour. The dichloride, when strongly ignited, is reduced to metal.

77. Reactions of the tetrachloride solution.—*Sulphuretted hydrogen* produces a brown colouration; after some time, more readily on heating, a black precipitate of sulphide PtS_2 is formed. This precipitate is somewhat difficultly soluble in yellow sulphide of ammonium; from the solution, which has a dark brown colour, it can be reprecipitated by acids. Platinum sulphide is not dissolved by nitric acid nor by hydrochloric acid, not even on boiling; nitrohydrochloric acid changes it into chloride. *Ferrous sul-*

phate does not reduce a solution of platinum tetrachloride, except on long-continued boiling. *Stannous chloride*, in presence of much free hydrochloric acid, produces a dark brown-red colour, owing to the formation of some dichloride, but *no* precipitate. *Chloride of ammonium* produces in not too dilute solutions a yellow crystalline precipitate of the composition $PtCl_4.2NH_4Cl$, little soluble in water, and still less so in alcohol. The double chloride when ignited leaves a spongy mass of platinum.

Most platinum compounds are decomposed on ignition, with separation of metallic platinum.

78. *Tungsten*,

as obtained by the reduction of tungstic acid in hydrogen at a high temperature, is an iron-grey powder which when pressed with a hard body acquires metallic lustre. Spec. grav. = 17·4. It is not fusible even in the strongest heat of the blowpipe or an ordinary furnace. At a red heat it decomposes water and is changed into oxide.

79. Tungstic trioxide WO_3 (usually called tungstic acid). The hydrates are white; the anhydrous oxide is a yellow powder. Tungstic acid is insoluble in aqueous acids, but soluble in caustic alkalies. After ignition it is insoluble in ammonia. Alkaline tungstates are soluble in water; the other salts are mostly insoluble. By treatment with hydrochloric acid tungstates, generally, are decomposed, with separation of tungstic acid.

Reactions of Tungstates.—In solutions of alkaline tungstates, *hydrochloric acid* gives a white precipitate, which on heating becomes yellow. When a solution of alkaline tungstate is mixed with *sulphide of ammonium*, and the mixture acidified, a brown precipitate of sulphide is formed; a part of the metal, however, generally remains in solution as a lower oxide, which imparts to the supernatant liquid a blue colour. The sulphide is soluble in sulphide of ammonium, and, from the solution, reprecipitated by acids. If a tungstate is treated with *zinc and hydrochloric acid* a blue solution is formed, containing tungstate of tungstic oxide.

80. Tungstic oxide WO_2 is produced by reducing the acid WoO_3 by hydrogen at a *dull red heat*. It is a brown substance insoluble in acids. By the action of hydrogen, at a *strong red heat*, it is reduced to metal. When heated in air or treated with nitric acid it is changed into the acid.

81. Dry-way tests.—Tungsten oxides impart to the microcosmic *salt*-bead in the reducing flame a blue (in presence of iron, a blood red) colour; in the oxidizing flame the bead is decolourized. The borax-bead in the reducing flame becomes yellow, in the oxidizing flame colourless. Tungsten oxides, when fused with small quantities of carbonate of soda or cyanide of potassium on charcoal, yield a grey powder of metal. With large quantities of alkali *no* metal is formed.

82. *Molybdenum,*

as obtained by reducing a molybdic oxide in hydrogen, forms a grey powder acquiring metallic lustre when pressed with a hard body, fusible only at the highest temperatures producible in a blast furnace. The fused metal is as hard as topaz, and has a specific gravity of 8·6. When heated in air it is slowly oxidized, first to dioxide, at last to trioxide. Excess of hot nitric acid converts it into trioxide.

83. **Molybdic 'acid'** MoO_3 is a white powder, fusible at a red heat to a dark yellow liquid; when heated to redness in a current of air it sublimes in colourless crystals. If not previously ignited, it is slightly soluble in water and easily soluble in hydrochloric acid. Whether ignited or not, it dissolves in the aqueous hydrates of potassium, sodium, and ammonium; the solutions contain molybdate. The rest of the molybdates are mostly insoluble in water.

84. **Reactions of solutions of alkaline molybdates.**—*Hydrochloric acid* gives a white precipitate, soluble in excess. If *metallic zinc* be added, the mixture, by gradual reduction of the molybdic acid, becomes first blue, then green, then dark brown, and at last a black precipitate of the oxide MoO is produced. *Sulphuretted hydrogen* precipitates acidified solutions but slowly; the brown precipitate is trisulphide MoS_3. A part of the metal remains dissolved as a lower oxide, imparting to the filtrate a blue or green colour. A more complete precipitation can be effected by adding to an alkaline solution sulphide of ammonium (or saturating it with sulphuretted hydrogen), and then acidifying with hydrochloric acid. The precipitated sulphide is soluble in sulphide of ammonium, and from the solution is reprecipitated by acids. If a solution of the ammonium salt is mixed with excess of nitric acid and a trace of a *phosphate*, the mixture on heating deposits a yellow precipitate, insoluble in excess of the acid molybdic solution, but soluble in solutions of phosphates. (Compare chapter on phosphoric acid.)

85. **Molybdic oxide** MoO_2 as formed by igniting ammonium molybdate in a close vessel, or by heating the hydrate *in vacuo*, is a red brown substance, nearly insoluble in hydrochloric and in sulphuric acid, left unchanged also by a solution of potash. When heated in air or treated with nitric acid it is changed into the trioxide.

86. Blowpipe tests.—Molybdenum oxides, when fused together with borax in the *oxidizing* flame, yield beads, more or less intensely yellow in the heat, but almost colourless after cooling. In the *reducing* flame the beads become dark brown ; if much molybdenum is present, a part of it separates out in the form of brown flakes of MoO_2. The *microcosmic salt* bead, after *oxidation*, is greenish, but becomes almost colourless after cooling. In the reducing flame it assumes a dark green colour, which on cooling loses intensity but gains in purity.
Molybdic acid, when heated on *charcoal* in the *oxidizing* flame, first melts, and is then partly volatilized, forming a sublimate which is yellow in the heat but colourless after cooling. The deposit, if again touched with the flame, is partly volatilized and partly converted into non-volatile MoO_2, which exhibits a dark red colour (after cooling) and metallic lustre. When heated, on charcoal, in the *reducing* flame, the acid mostly creeps into the charcoal, and is there reduced to metal, which, on elutriation, is obtained as a grey powder.

Regarding *Vanadium*, see appendix to *Summary*.

Summary and Additions.

Properties of the metals Arsenicum, Antimony, Tin, Gold, Platinum.

87. Behaviour to heat.—(Within the range of temperatures producible with a smokeless gas or blowpipe flame.)

a. In absence of air.

Arsenicum, easily volatilized below a red heat, even from under a flux.

Antimony, if indirectly heated, as in a sublimation-tube, not volatilized. In a current of gas it volatilizes slowly at a red heat, but not if covered with a molten flux, as potassium cyanide, KCy. It is easily volatilized if directly exposed on charcoal to a reducing blowpipe flame.

Tin, not volatile, if indirectly heated, not even in current of gas. If heated on charcoal with a blowpipe flame, it is volatilized, but much more slowly than antimony.

88. *b. In presence of air.*

Arsenicum, easily changed into volatile, crystalline, arsenious anhydride, As_2O_3.

Antimony, if heated in a draught-tube, is oxidized, though less easily than arsenic, and is changed, first into volatile antimony teroxide, Sb_2O_3, and then into the non-volatile tetroxide, Sb_2O_4. If directly heated on charcoal with a blowpipe flame, it is rapidly oxidized.

Tin, if indirectly heated, is scarcely oxidized. If directly exposed to a blowpipe flame it is oxidized, but much more slowly than antimony.

Gold and Platinum, under the circumstances stated, are non-volatile and non-oxidizable. Platinum is also non-fusible. The oxides, and most other compounds of gold and platinum are, by heating, reduced to metal.

89. Action of Nitric Acid.

$\left.\begin{array}{l}\textbf{Gold,}\\\textbf{Platinum,}\end{array}\right\}$ not changed.

Arsenic, changed first into arsenious (As_2O_3) and then into arsenic oxide (As_2O_5), both of which are soluble.

Antimony, Tin, changed into, respectively, antimonic anhydride, Sb_2O_5, and stannic anhydride, SnO_2, both of which are insoluble in water and in nitric acid.

Reactions of solutions of salt-like compounds (e.g. chlorides, oxides, etc.) of the metals named.

90. Sulphuretted hydrogen, in presence of free acid, and supposing the latter to be diffused in a sufficiency of water, precipitates the metals completely as sulphides, which sulphides are soluble in sulphide of ammonium, and from such solutions may be reprecipitated by addition of acids.* To separate, therefore, the arsenic group from the copper group (and all other metals), we precipitate both groups together by means of sulphuretted hydrogen, wash the sulphides, treat them at a gentle heat with sulphide of ammonium (which, on account of the possible presence of stann*ous*, platinum, and gold sulphides, must contain an excess of sulphur), filter, and acidify the filtrate with hydrochloric acid, when the sulphides of the arsenic group will be separated out along with free sulphur. To effect as complete a separation as possible, the digestion with sulphide of ammonium should be done at a gentle heat and be repeated several times. A precipitate obtained in the way described may consist merely of sulphur (in which case it presents a milky appearance, while even a small admixture of a metallic sulphide renders it curdy and discoloured); on the other hand, it is liable to contain small quantities of sulphide of copper. See § 17.*

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* For precautions to be observed to secure the speedy and complete precipitation of certain metals, consult §§ 46, 77, 56, 45, 26, 36; also last chapter of Div. II.

Solubility relations of the precipitated sulphides.

91. *Fuming hydrochloric acid*, at a gentle heat—
dissolves . . . sulphides of antimony and tin.
scarcely acts on . . „ „ arsenic.
does not dissolve . . „ „ gold and platinum.

92. A concentrated solution of *sesquicarbonate of ammonia* dissolves As_2S_3, which can be reprecipitated by acids, scarcely acts on sulphides of Sb, Sn, Au, Pt, nor on free sulphur. (SnS_2 is perceptibly soluble.)

93. The *dry sulphides* when heated in presence of air (projected in small successive portions into a red-hot porcelain crucible) behave as follows:—Sulphides of
Arsenic, are volatilized.
Antimony, changed into Sb_2O_4.

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* This source of error is avoided, if, instead of sulphide (or polysulphide) of ammonium, the corresponding sodium or potassium compound, or caustic potash be used for the extraction of the arsenic group from the H_2S-precipitate. It is however to be observed that the sulphides of potassium and sodium, the salts R_2S at least, dissolve *mercuric* sulphide, and that, from a solution of sulphide of *arsenic*, *antimony*, or *tin* in *caustic alkali* (which of course must contain a *part* of the metal as an *oxygen* compound), hydrochloric acid alone will *not* always precipitate the whole of the metal as sulphide. In case of arsenic pentasulphide, As_2S_5, for instance, part of the arsenic at least will remain dissolved as arsenic acid; thus:—$As_2S_5+8K_2O=As_2O_5.3K_2O+5K_2S$. Of the $5K_2S$ every 3 unite with As_2S_5 to form a thio-salt, which, on addition of acid, gives sulphide of arsenic, with evolution of sulphuretted hydrogen, most of which will *not* act on the arsenic acid, but will escape.

Tin, changed into SnO_2.
Platinum, Gold, } reduced to metals.

94. When *fused with nitrate of soda and carbonate of soda*, the sulphides of

Arsenic, are changed into sodium arseniate, Na_3AsO_4, which is soluble in water.

Antimony: changed into sodium meta-antimoniate, nearly insoluble in water, less soluble still in dilute alcohol; insoluble also in caustic soda.

Tin: changed into stannate of sodium, little soluble in water or dilute alcohol, but soluble in caustic soda (which may have been formed from the nitrate by overheating.)

Gold *Platinum* { reduced to metals. Platinum is dissolved by fused caustic alkali. See § 75.

95. The *oxides* of arsenic, antimony, and tin, when *fused* with *cyanide of potassium*,* are reduced to metals. If the experiment be performed in a sublimation-tube, then in case of *tin* or *antimony* the metal forms a *non*-volatile regulus; while, in case of *arsenic*, the metal is completely *volatilized* and obtained as a *mirror*. The volatilization of the arsenic is not interfered with by the presence of even *large* quantities of oxides of metals of the potassium and barium groups, of magnesium, bismuth, or antimony, or of moderate quantities of the oxides of manganese, tin, aluminium; while the rest of the oxides of the *copper* and *iron* groups, being all, by the action of the reagent, reduced to metals, the lower arsenides of which *cannot* be decomposed by mere heating, if present in sufficient quantities, *prevent* the formation of an arsenic mirror. In any case, a part of the arsenic vapour, by the action of the air in the sublimation-tube, will be burned into trioxide; hence, in case of small quantities of arsenic, the reduction had better be effected (within a horizontally placed tube, which should be about five m.m. wide inside) in a *slow* current of dry *carbonic acid.* If the exit-end of the tube is drawn out to a long tail about one and a half m.m. wide, and care be taken first to thoroughly drive off every trace of *moisture*, and to bring that part of the tube which is between the mixture and the narrow tail to dull redness before effecting the reduction, then as little even as one-fourth of a milligramme of arsenicum will give a distinctly visible mirror.—(*Fresenius.*)

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* Or, what is generally more convenient, a mixture of one part of the cyanide and three parts of dry carbonate of soda.

96. The *sulphides* of arsenic, antimony, and tin are also reduced by *cyanide of potassium* (with formation of sulphocyanate), but a part of the metal always remains as a non-reducible sulpho-salt. Hence arsenic sulphide, when mixed with a sufficiency of free sulphur, may fail to give a mirror.

97. Action of nascent hydrogen (*zinc and hydrochloric or sulphuric acid*) **on solutions of the oxides or chlorides of the arsenic group** :—

Tin, **Gold,** **Platinum,**	are precipitated as metals.
Arsenic, **Antimony,**	are partly precipitated as metals, and partly evolved as gaseous hydrides, AsH_3 and SbH_3.

In the case of antimony a small proportion of metal only is changed into hydride.

Applications of this reaction.

98. I. **Detection of Arsenic or Antimony.**

(*Marsh's test;* see § 48 and § 49.)

Marsh's test is more delicate for arsenic than for antimony. In either case, the more of the metal is changed into hydride the greater the quantity of free acid present; hydrochloric probably produces more than sulphuric acid.

99. Difference of arsenic and antimony stains.—Arsenic stains are generally bright, and have a metallic lustre; those of antimony are usually dull and sooty-looking.

Both stains, when gently heated with yellow sulphide of ammonium, are dissolved; the solution, after evaporation, leaves,

In the case of *arsenic:* yellow sulphide, insoluble in strong hydrochloric acid.

In the case of *antimony:* brick-red sulphide, easily dissolved by strong hydrochloric acid.

Arsenic stains are readily dissolved by a solution of bleaching powder; antimony stains cannot be thus dissolved.

Both stains when heated with nitric acid are dissolved; the solution, when evaporated, leaves,

In the case of *arsenic*, a residue of As_2O_3 or As_2O_5, the solution of which in water, when mixed with nitrate of silver, and very cautiously saturated with dilute ammonia, gives a yellow or brick-red precipitate of, respectively, arsenite or arseniate of silver, generally the latter.

In the case of *antimony*, the residue contains Sb_2O_3 (beside Sb_2O_5), and when treated with nitrate of silver and excess of ammonia gives a black precipitate of antimoniate of suboxide of silver.

100. Difference of arsenic and antimony mirrors.—The antimony mirrors are usually more metallic-looking than the arsenic ones. The arsenic mirror is by far the more volatile. Antimony *melts* before volatilizing. When the parts of the glass tubes containing the mirrors are heated within wide test-tubes of hard glass, the metals are oxidized. Arsenic yields a very volatile crystalline sublimate of As_2O_3; antimony yields, ultimately, a non-volatile amorphous deposit of Sb_2O_4. (See §§ 42, 51, 88.)

101. 2. Detection of Arsenic and Antimony.

(When present together.)

When a solution containing both arsenic and antimony is subjected to Marsh's process, the arsenic is chiefly contained in the first, while antimoniuretted hydrogen predominates in the latter portions of the gas, so that it is sometimes possible to obtain, separately, stains of nearly pure arsenic and pure antimony. But this method of fractionating is not sure to succeed. A real separation of the metals, in the hydrides, can be effected by passing the gas through a solution of nitrate of silver, when both hydrides are decomposed; the arsenic passes into solution as As_2O_3, while the antimony is precipitated as antimonide of silver.

$$2AsH_3+12AgNO_3+3H_2O=12Ag+12HNO_3+As_2O_3$$
$$2SbH_3+6AgNO_3=6HNO_3+2SbAg_3.$$

If the filtrate be cautiously neutralized with ammonia, and, if necessary, some nitrate of silver added, a yellow precipitate of silver arsenite is obtained ($2Ag_2O.As_2O_3$).—(*Otto.*) To detect the antimony, *A. W. Hofmann* recommends to wash the precipitate with hot water, and then to boil it with a solution of tartaric acid, when the antimony (*i.e.* that part which by the action of the air has been oxidized?) passes into solution, and after filtration can be detected by means of sulphuretted hydrogen. According to our experience, a safer method is to digest the washed precipitate with yellow sulphide of ammonium, when the antimony dissolves as thio-salt. The filtered solution when evaporated to dryness at a gentle heat leaves a red residue (Sb_2S_5), which is instantaneously decolourized by even cold fuming hydrochloric acid. But even with this method the detection of the antimony is not by any means so easy as that of the arsenite in the filtrate. Hence a negative result obtained regarding the former is all the better for being confirmed by other independent processes.

We here remind the beginner that Marsh's test applies only to acid solutions of the *oxides* of arsenic and antimony, and especially does not succeed with sulphides and sulpho-salts. The presence of considerable quantities of oxidizing agents, such as nitric or chloric acid, should be avoided.

If, besides arsenic and antimony, there are other metals present which are precipitated by zinc (as tin, lead, bismuth, mercury), they will more or less interfere with the formation of the hydrides.

102. 3. Detection of Arsenic, Antimony, and Tin.

If, in a solution containing these three metals, the tin does not predominate too much, arsenic and antimony can be detected by Marsh's test, as above described. The tin remains in the residue as a metallic precipitate, along with, generally, the greater part of the antimony and some of the arsenic. In this case it will be found expedient to modify the *modus operandi*, in so far as to use very little zinc (5 grammes, or less), to substitute hydrochloric for sulphuric acid, and to collect the gas evolved, previously to operating upon it, over water in a glass gasometer. (1 gramme of zinc gives about 0·36 litre of hydrogen.) The operation is continued until all the zinc is dissolved, and the solution (A) decanted from the precipitate, replaced by pure hydrochloric acid, and the mixture heated for some time so as to dissolve the tin (sol. B), while the antimony, and, generally, impurities from the zinc, remain. The gas evolved during the solution of the tin may contain arseniuretted hydrogen, and is therefore collected in the gasometer. Thus the bulk of the arsenic and some of the antimony are obtained as hydrides, which can be examined as in 2; the tin is contained in solutions A and B as $SnCl_2$, which can be tested for by mercuric chloride, or, after partial oxidation with $FeCl_3$, by *chloride of gold*. The antimony can more easily be detected in the residue left undissolved by hydrochloric acid than in the gas. For this purpose the residue is washed with water, digested with yellow sulphide of ammonium, and the filtered solution evaporated; antimony sulphide remains as a brick-red mass, soluble in fuming hydrochloric acid.

103. Examination of a mixture of precipitated sulphides of the Arsenic group.

From what is given in the preceding paragraphs, it would appear to be easy to deduce methods for the exact separation from one another of the five metals (§ 87) potentially present in such a mixture; but practically it is not so, the reason being that a *mixture* of the metals in question—whether they are given as such, or as sulphides or oxides, etc.—when subjected to the action of reagents will in general *not* behave so as if each of the constituents was treated for itself in a separate vessel. Thus, for instance, in the case of an alloy of tin and arsenic, the two metals *can not* be separated completely by even prolonged and intense heating. If we attempt a separation by oxidation with nitric acid, and subsequent treatment of the oxides with water, we obtain a residue containing both stannic *and* arsenic acids in chemical combination with each other, and a solution containing *at best* only a part of the arsenic. It would be easy to give further illustrations. The exact separation from one another of the metals we have here to deal with is, in fact, one of the most difficult problems of analysis, which has not yet by any means received a satisfactory solution. For the purpose of a *qualitative* analysis, however, it is obviously sufficient to effect what is called a '*qualitative separation*,' *i.e.* by a proper combination of processes, to extract the bulk of each metal in the state of a definite compound, sufficiently pure to be identified by its characteristic tests. What methods we should employ, and how we should combine them with one another, depends on the particular case we have to deal with, the quantity of material we have at our disposal being evidently one of the first points to be considered. To beginners who have not yet learned to invent their own methods, we recommend the following series of procedures:—

104. Starting with a mixture of *precipitated sulphides*, proved to be free from metals of the copper and iron groups, first dry a portion of the precipitate, and carefully roast it on an inverted porcelain crucible lid. If it burns off completely, it can contain only *arsenic*, which in another portion of the precipitate is readily detected by boiling the sulphide with hydrochloric acid and a little nitric acid or chlorate of potash, and then searching for *arsenic acid* by means of *magnesia mixture* (§ 46), or by applying Marsh's process (§§ 48, 49, 99, 100). If there is a fixed residue left (SnO_2, Sb_2O_4, and more or less of As_2O_3), then, however little it may be, it will suffice for the application of Bunsen's flame-tests for antimony and tin. To test for *antimony*, place a little of the roasted mass on one end of an *asbestos stick*, and expose it to the action of the luminous 'tip' of the flame of a Bunsen's lamp, while, with the other hand, you hold a porcelain basin into the flame, close over the specimen. If the basin gets coated with a metallic stain, *insoluble in bleaching-powder solution*, this proves the presence of antimony. The tin-test is described in § 71; a negative result in case of the antimony-test, and a positive in that of the tin, must not be considered as perfectly conclusive.

Whatever may be the results of these preliminary tests, and supposing even gold and platinum to be *known* to be absent, it is always better to proceed to an approximate separation of the metals from one another, and to identify each of them for itself. For this purpose,

105. Allow the rest of the precipitate to drain as completely as possible, treat it, at a gentle heat, with *fuming hydrochloric acid* until there is no longer any action, then remove the dissolved sulphuretted hydrogen by means of a current of carbonic acid (*i.e.* pass carbonic acid through the mixture, until a drop of it no longer gives a black precipitate with copper vitriol), dilute and filter. Then, substantially,

The Precipitate

contains the *arsenic*, *gold*, *platinum*, and perhaps traces of copper, antimony, and tin, as *sulphides*. Treat the precipitate at about 80° with a solution (saturated in the cold) of *sesquicarbonate of ammonia*. The *solution* contains the arsenic, which by acidification of the filtrate with HCl, and addition of H_2S, can be precipitated as As_2S_3. The As_2S_3 can be identified by means of cyanide of potassium (§ 95) or otherwise. *The residue* (S, Au^2S^3, PtS_2) is oxidized by roasting and subsequent fusion with nitrate of potassium, at the lowest possible temperature, and the mass treated with water. The solution may contain the potash salts of Sb_2O_5, SnO_2, As_2O_5; the residue consists of metallic *gold and platinum*.

(*Vide* infra.)

The Filtrate

contains the bulk of the *antimony* and *tin* as chlorides $SbCl_3$, $SnCl_2$, $SnCl_4$, and perhaps (in absence of SnCl) some arsenic, which, after due concentration, may be searched for by Bettendorf's test (see § 47). Take a portion of the solution, evaporate to expel the greater part of the free acid, and test for *antimony* by means of zinc and platinum (§ 56). To test for *tin*, dissolve the whole of the zinc by addition of hydrochloric acid, and search for tin as shown in § 102. Or, better, examine the original filtrate in a small Marsh's apparatus according to § 102.

106. Separation of Gold and Platinum from other metals and from each other.

In the examination of a solution of salts, *gold and platinum* should be separated out from the first instead of being allowed to find their way into the arsenic-group precipitate. In case of a solution of chlorides free from oxidizing agents (*e.g.* nitric acid), and containing as little as possible of free acid, this can generally be effected :

1. By adding to the solution an excess of *formiate of soda* along with some carbonate of soda, and boiling for a considerable time, when the two noble metals are thrown down (as such) as constituents of a precipitate, from which all that is not gold or platinum (or *mercurous chloride*) can be extracted by means of hot hydrochloric acid.

2. (*If gold is either absent or associated with a sufficiency of platinum*) by treating the solution (at the temperature

of a water bath) with *hydrogen.* If matters be arranged so that the solution presents a large surface to a continuously renewed atmosphere of hydrogen, the *platinum* and *gold*, in the course of a day or so, are completely reduced and precipitated.—(*Brunner; W. D.*) To avoid explosions, the hydrogen must be displaced by *carbonic acid* before the flask is opened. If, even a neutral, dilute solution of *pure chloride of gold* is subjected to this process, a very insignificant fraction of the metal only is precipitated.

To separate the two metals from each other, convert them (by treatment with aqua regia, etc.) into *neutral* chlorides, dissolve these in the least quantity of water, and add a concentrated solution of *sal-ammoniac* and 2–3 vol. of alcohol: the platinum is precipitated (after some time) as yellow crystalline $PtCl_4.2NH_4Cl$—which must be washed with *alcohol;*—gold passes into the filtrate, from which it can be obtained by evaporation to dryness and ignition. The gold remains as such, and after reconversion into chloride can be identified by means of stannous chloride (§ 73).

107. Bloxam's method for the qualitative separation of Arsenic, Antimony, and Tin

supposes the metals to have been precipitated, from the solution of their sulphides in sulphide of ammonium, by hydrochloric acid, and consequently to be given as As_2S_3, or As_2S_5, Sb_2S_3 or Sb_2S_5, and SnS_2 respectively. The precipitate is digested at 80° C. in a concentrated solution of *sesquicarbonate of ammonia*, which extracts all the *arsenic* and some tin. From the filtrate the two metals are precipitated, by acidification, as sulphides and identified; the arsenic by means of cyanide of potassium, the tin by roasting part of the precipitate in a porcelain crucible, when the tin remains as SnO_2, which is easily recognised by flame and blowpipe tests. The residue (Sb_2S_x and SnS_2) might be examined as shown in § 105, but *Bloxam's* method is to dissolve it in hot hydrochloric acid, with addition of the least quantity of nitric acid required for converting the metals into their highest chlorides, and then to boil with a large excess of sesquicarbonate of ammonia; if there is a precipitate, it contains the *whole of the tin* and part of the antimony; some of the latter, however, always passes into the filtrate, from which, after acidification, it can be precipitated by sulphuretted hydrogen.

108. The most exact method for the separation of Arsenic, Antimony, and Tin

is the following :—Dissolve the mixed sulphides in *sulphide of potassium*, add a large excess of aqueous *sulphurous acid*, and, after having digested the mixture at a gentle heat for some time, boil it down to about one-third of its original bulk, and filter. The filtrate contains the whole of the arsenic as arsenite, along with thiosulphate of potash; it is completely precipitated, as As_2S_3, by sulphuretted hydrogen. The precipitate contains the antimony and tin as sulphides, mixed with a considerable quantity of sulphur.—(*Bunsen.*). To separate these two metals, first convert them into the highest oxides (SnO_2, Sb_2O_5), fuse these in a silver dish with a large excess of *caustic soda*, and treat the fused mass with cold water. After complete disintegration add one-third of the volume of the mixture of alcohol of 0·83 sp. grav., allow to settle, and filter. The precipitate, which contains the whole of the antimony as meta-antimoniate of soda, must be washed with a mixture of equal volumes of alcohol and water. From the *filtrate* which contains the whole of the tin as stannate (and all the arsenic, if present), the metal may be precipitated either by excess of *sulphuric acid* (§§ 67-69) as oxide, or—after saturation with sulphuretted hydrogen—by means of acetic acid, as sulphide. [If this precipitate contains arsenic, this can be completely eliminated by heating the dry sulphides in a current of dry sulphuretted hydrogen; the arsenic sulphide is completely volatilized, and what (of the vapours) does not condense in the colder parts of the reduction-tube, can be collected in aqueous ammonia.]—(*H. Rose.*) A complete oxidation of the sulphides of antimony and tin presents great difficulties. One of the methods recommended for the purpose is to treat the *dried* sulphides in the heat with *fuming* nitric acid (of 1·5 spec. grav.), but this is an extremely troublesome operation. For the purposes of an exact qualitative analysis it would probably be sufficient to dissolve the mixed sulphides in aqua regia, to dilute, filter off the sulphur, to evaporate repeatedly with nitric acid (of 1·4 sp. gr.)—ultimately very nearly to dryness, to moisten with caustic soda solution, evaporate to dryness, in a silver dish, and to fuse with additional caustic soda.

109. Regarding *tungsten*, *molybdenum*, and *vanadium*,* we will confine ourselves to giving a tabular statement of reactions, by means of which any *one* of these metals, if it should have found its way into an arsenic group precipitate, may be searched for and identified.

The sulphides of the metals named, when *roasted*, are converted into their highest oxides, viz. :—

Molybdic Acid.	Tungstic Acid.	Vanadic Acid.
MoO^3	WoO_3	V_2O_5
White, fusible. Can be sublimed at a red heat in a current of air.	Yellow, infusible. Absolutely non-volatile.	Dark-red, fusible. Non-volatile. Soluble in 1000 parts of H_2O. Solution yellow.
Soluble in ammonia, even after ignition; solution colourless.	After ignition, insoluble in ammonia.	Soluble in ammonia, even after ignition.

The three acids, if fused with carbonate of soda, are converted into sodium salts, soluble in water. The solution of the sodium salt is,

Colourless.	Colourless.	Colourless.

If mixed with hydrochloric acid, the solutions behave as follows—

White precipitate; soluble in excess of hydrochloric acid, and also in much water.	White precipitate in the cold, which becomes yellow on heating; insoluble in hydrochloric acid.	No precipitate from dilute solutions; the liquid becomes intensely red (like an acid chromate).

If the mixtures (containing the free acids in solution, or as precipitates) are treated with zinc (nascent hydrogen), the acids are reduced to lower oxides, and intensely coloured liquids are produced. The colours are—

First blue, at last dark brown.	Blue.	First green, then blue, at last violet.

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* This metal, on account of its *very* rare occurrence, is not noticed in the context. For a similar reason the platinum metals, except platinum itself, are entirely omitted.

C. IRON GROUP.

CHROMIUM, ALUMINIUM, IRON (URANIUM), COBALT, NICKEL, MANGANESE, ZINC (AND A NUMBER OF RARE METALS).

Chromium.

110. Metallic Chromium, as obtained by igniting a mixture of violet chromic chloride Cr_2Cl_6 and chlorides of sodium and potassium with zinc, forms a light green crystalline powder of spec. gr. 6·8.—(*Wöhler.*) It is more difficultly fusible than platinum; the fused metal is as hard as corundum.—(*Deville.*) When heated in air, it is very superficially changed into green chromic oxide Cr_2O_3. Dilute hydrochloric acid dissolves it readily, forming a blue solution of chromous chloride $CrCl_2$. It is not at all attacked by nitric acid, whether dilute or strong.

111. Chromous oxide, CrO, is scarcely known by itself. The salts derived from this oxide are very unstable; their solutions, when exposed to the air, or treated with oxidizing agents (nitric acid, free chlorine, etc.), are easily changed into chromic salts.

112. Chromic oxide Cr_2O_3, as prepared by gently heating the hydrate, is a dark green powder, which, when treated with acids, yields solutions of chromic salts (*e.g.* Cr_2Cl_6, $Cr_2(SO_4)_3$); when being strongly ignited, it becomes incandescent and is changed into another modification, which is almost absolutely insoluble in acids.

There are several *chromic hydrates.* They are all easily soluble in acids, forming solutions of chromic salts.

113. Chromic Salts.—There are two modifications of chromic salts; those of the one give green, and those of the other violet, solutions with water. Only the violet solutions yield crystalline salts, the green ones give amorphous masses.

Behaviour to reagents of solutions of chromic salts.—*Sulphuretted hydrogen.*—No change. *Sulphide of am-*

monium acts like ammonia, *sulphuretted hydrogen* being liberated. *Ammonia* precipitates hydrate (which in case of green solutions is greyish green, in case of violet ones greyish-blue), slightly soluble in excess of ammonia. When the excess of ammonia is boiled off, the dissolved oxide is reprecipitated. *Tartaric acid* (like many other non-volatile organic compounds) prevents the precipitation.

Potash (also soda) precipitates bluish-green hydrate ($Cr_2O_3.5H_2O$) soluble in excess of the reagents. When the green alkaline solution is boiled, the chromic hydrate is completely precipitated; on cooling, however, it partially redissolves. When the alkaline solution is heated with peroxide of lead PbO_2, a (yellow) solution of chromate of alkali R_2OCrO_3 is formed.

114. Chromic acid and chromates.—Chromium (and any non-volatile chromium compound) when fused with *carbonate or hydrate of alkali*, and *nitrate* or *chlorate of potash*, is converted into *chromate* CrO_3R_2O.

115. Chromic trioxide, CrO_3, forms crimson crystals which are easily soluble in water; the solution, if concentrated, is brown red, if dilute, yellow. When heated beyond 250° the teroxide loses oxygen and is reduced to Cr_2O_3. The real acid $CrO_3.H_2O$ is not known.

116. Chromates.—The normal alkaline chromates (R_2O CrO_3, *e.g.* K_2OCrO_3) are yellow, and dissolve in water with a yellow colour, which is so intense that it is shown even after very considerable dilution with water. The alkaline bichromates (R_2O2CrO_3) are garnet-red, and give red solutions. Of the rest of the chromates, the calcium, magnesium, and the acid strontium salts are soluble, the others are mostly insoluble in water, but soluble in mineral acids.

117. *Behaviour of solutions of alkaline chromates to reagents.* —*Barium chloride* precipitates $BaCrO_4$, a yellow powder, insoluble in water, difficultly soluble in dilute nitric or hydrochloric acid. *Acetate of lead* precipitates lemon-yellow $PbCrO_4$, insoluble in dilute nitric acid, soluble in caustic potash. *Nitrate of silver* precipitates red chromate of silver Ag_2OCrO_3, nearly insoluble in water, soluble in dilute nitric acid, and in ammonia. *Mercurous nitrate* precipitates dark brick-red $4Hg_2O.3CrO_3$, which, when boiled with nitric acid, is changed into red crystalline Hg_2OCrO_3. The precipitate, when ignited, leaves green chromic oxide, oxygen and mercury vapour going off.

118. *Chromic* acid and *chromates* can *be reduced to chromic* salts, in a great many different ways. *Solutions* by means of (*a.*) *Sulphuretted hydrogen and free acid* (with precipitation of sulphur); (*b.*) *Stannous chloride* (with formation of stannic chloride $SnCl_4$); (*c.*) *Nascent hydrogen* (*e.g.* zinc and hydrochloric acid); these reactions go on in the cold; (*d.*) By being heated with *free acid* and *alcohol* (the alcohol being converted into aldehyde, chloride of ethyl, and other volatile products).

Solid chromates can be reduced, (*a.*) by being boiled with *hydrochloric acid* (formation of free chlorine and chromic chloride); (*b.*) by being heated with *concentrated sulphuric acid* (formation of chromic sulphate and oxygen).

119. Blowpipe-test.—Chromic oxides, when fused with borax, in either flame, give *green* beads. See also § 114.

120. Chromium, in any state of combination, even if forming part of the most complex mixture, is easily *detected* by fusing the substance with carbonate and nitrate of potash. The metal is converted into *alkaline chromate*, which can be recognised by the yellow colour and the reactions of its aqueous solution. If the solution should be *green* from *manganate* this can easily be eliminated by addition of a few drops of alcohol, heating and filtering. The manganese is completely precipitated, the chromate remains unchanged. Minute traces of chromic acid, too small to produce a distinct colour, may be detected by means of a solution of *peroxide of hydrogen in ether*, which reagent, when shaken with the acidified solution of a *trace of chromate*, assumes an intense *blue* colour.

If, in the application of this test, the *aqueous liquid* assumes a *brownish-red* colour, this proves the presence of *vanadic acid*.—(*Werther.*) In this case however the non-appearance of the blue colour in the ethereal layer does *not* prove the absence of CrO_3.

Aluminium.

121. **Aluminium** is a ductile metal of the colour and lustre of tin, and about as hard as pure silver. It melts at about 700°. In air, at ordinary temperatures, it does not change, and, even at a red heat, it is very little oxidized. It does not decompose water, not even at a red heat. *Hydrochloric acid* dissolves aluminium, with evolution of hydrogen. Dilute *sulphuric acid* does the same, but more slowly. The solutions contain aluminic salt (Al_2Cl_6, resp. $Al_2(SO_4)_3$). *Nitric acid*, whether concentrated or dilute, does not attack the metal. *Caustic potash* (also *soda*) dissolves it, with evolution of hydrogen and formation of *aluminate*.

122. **Aluminic oxide** Al_2O_3 (Syn. *Alumina*) is a white powder which, if not previously ignited, dissolves in acids, with formation of aluminic (alumina) salts. After strong ignition it is very difficultly attacked by acids. *Native* alumina (sapphire, ruby, oriental topaz, collectively 'corundum'—; emery) is absolutely insoluble in acids. The insoluble varieties of alumina, if *very finely powdered* and fused with *bisulphate of potash*, are changed into aluminic sulphate, soluble in water. When fused with *caustic potash* (in a silver vessel) they are converted into (soluble) aluminate of potash. *Aluminic hydrate*, as obtained by precipitating the chloride with ammonia, is a gelatinous, very bulky precipitate, which, however, shrinks greatly on being dried. It dissolves in dilute acids, and also in aqueous caustic potash or soda, but is only slightly soluble in ammonia.

123. *Behaviour of solutions of aluminic salts to reagents.*—*Sulphuretted hydrogen.*—No action. *Sulphide of ammonium* acts like ammonia, sulphuretted hydrogen being liberated. *Ammonia* precipitates (colourless, gelatinous) hydrate or basic salt, slightly soluble in excess of the reagent;

if the excess of the ammonia be boiled off, the dissolved alumina is reprecipitated. The precipitate is quite insoluble in water and in solutions of ammonia salts, also in sulphide of ammonium; hence this reagent is a better precipitant, than caustic ammonia, for alumina. *Caustic potash* (also soda) gives a precipitate of hydrate, soluble in excess of the alkali; the solution remains clear on boiling, but if heated with excess of chloride of ammonium (*i.e.* more than 1 'NH_4Cl' for every 1 'KHO' used for dissolving the precipitate), the alumina is completely reprecipitated.

Oxalic acid gives no precipitate with aluminic salts.

A solution of the *sulphate or chloride*, if mixed with *sulphate of potassium* or of *ammonium*, and sufficiently concentrated by evaporation, deposits, on cooling, octahedral crystals of 'Alum' ($Al_2(SO_4)_3.R_2SO_4.24H_2O$).

124. *Phosphate of alumina* possesses about the same solubility relations as alumina itself; its solutions in acids (hydrochloric, nitric, sulphuric) behave to soda, potash, ammonia, sulphide of ammonium, and its solution in potash to chloride of ammonium, like the corresponding solutions of the oxide; only the precipitate is, in each case, *phosphate* of, instead of *pure*, alumina.

125. Blowpipe test.—Alumina, if ignited on charcoal, moistened with *nitrate of cobalt*, and again ignited, give a *blue infusible* mass. The presence of phosphoric or arsenic acid, and of barium, magnesium, iron, calcium, in moderate quantities, does not interfere with this reaction.

126. *Note.*—Precipitates of *silicic acid* and of *phosphate of lime* present pretty much the same appearance as, and therefore are liable to be confounded with, alumina. *Silicic acid* is distinguished from alumina by its *not* being rendered soluble by fusion with alkaline bisulphate; *phosphate of lime*, by its insolubility in caustic potash, and the fact of its hydrochloric solution when mixed with *sulphuric acid* and *alcohol*, giving a precipitate of sulphate of lime and a solution of phosphoric acid.

127. Beryllium, Zirconium, Cerium, Lanthanum, and Didymium, are comparatively rare metals. Their salts behave to *sulphuretted hydrogen*, *sulphide of ammonium*, and *ammonia*, like those of aluminium. The following table shows how these metals (beryllium and zirconium individually, and cerium, lanthanum, and didymium as a class) can be distinguished from, and detected in presence of, aluminium :—

	Beryllium.	**Zirconium.**	**Cerium, Lanthanum, Didymium.** (Cerite-Metals.)
Occurrence.	Beryll, Euklas, Phenakite.	Zircom, some kinds of Garnets.	Cerite (hydrated Silicate of Cerite-Oxides).
Oxalic acid.	No precipitate.	Precipitate of oxalate, insoluble in oxalic acid.	
Caustic Potash precipitates:	Hydrate, soluble in potash; on continued boiling the hydrate is reprecipitated.	Hydrate, insoluble in caustic potash.	
Behaviour of hydrates to boiling solution of *salam oniac.*	Hydrate dissolves.	Hydrate does *not* dissolve.	Hydrates of lower oxides dissolve, the higher ones do not.
Sulphate of Potash	and Beryllium sulphate form *no* difficultly soluble '*Alum.*'	Precipitates a double salt, which is nearly insoluble in water and in dilute acids.	A solution of potassium sulphate saturated in the heat precipitates double sulphates, insoluble in solutions of potassium sulphate, but soluble in dilute hydrochloric acid.
Carbonate of Ammonia.	Hydrates dissolve in a concentrated solution of the reagent. (*Alumina* does not.)		Precipitated Ce^2O^3 is soluble in the reagent.

For further information regarding these metals and the still more rarely occurring elements, Thorium, Yttrium, Erbium, see Rose's *Handbuch*, new edition by Finkener.

Titanium.

128. Occurs in nature as Rutile, Anatas, Brookite (native TiO_2); as titaniferous iron ($FeOTiO_2$), etc. The slags formed in iron-smelting occasionally contain copper-coloured cubes of a compound $TiCy_2.3Ti_3N_2$, which for a long time were mistaken for metallic titanium, until *Wöhler* found out their real nature.

129. *Titanic dioxide.*—TiO_2 (Syn. Titanic acid). The native oxide, and also the artificially prepared oxide after strong ignition, is insoluble in hydrochloric and dilute sulphuric acids, very difficultly soluble in concentrated sulphuric acid, easily soluble in hydrofluoric. The insoluble oxide can be got *into solution* (1.) by fusing it with *bisulphate of potash*, and dissolving the fused mass in cold water; (2.) by fusion with *alkaline carbonate;* the fused mass, when treated with water, leaves *acid titanate*, insoluble in water, but soluble in cold concentrated hydrochloric acid.

130. The *acid solutions* behave as follows :—(1.) When *diluted* with water and *boiled*, they deposit *titanic acid* as a white precipitate. The precipitate obtained from the hydrochloric solution goes through the filter, which however can be prevented by addition of chloride of ammonium. (2.) *Caustic alkalies* (potash, soda, ammonia) and ammonium sulphide precipitate a gelatinous hydrate $2TiO_2.H_2O$. The precipitation is prevented by tartaric acid. The hydrate, when washed with *cold* water, remains soluble in cold dilute acids. (3.) When the hydrochloric or sulphuric solution is treated with *zinc*, a chloride corresponding to a lower oxide Ti_2O_3 is formed, and the solution assumes a blue or violet colour; after prolonged action a blue precipitate of titanous hydrate is formed.

131. *Blowpipe tests.*—Oxide of titanium and *microcosmic salt*, when fused together in the oxidizing flame, give a bead, which is yellowish in the heat and colourless in the cold. In the reducing flame (more readily on addition of tin) the bead becomes, after cooling, violet; in presence of iron, blood-red. TiO_2, when fused on charcoal with KCy, yields *no* metal.

132. *To separate titanic acid from iron*, in an acid solution of the two oxides, it is not enough to boil the solution, because the precipitate of titanic acid thus produced invariably carries down ferric oxide; it is better to precipitate the two metals by means of *sulphide of ammonium* (ppte. FeS and $TiO_2.xH_2O$) and to treat the precipitate with aqueous *sulphurous acid*, which dissolves the ferrous sulphide and leaves pure titanic acid.

Iron.

133. Pure **metallic iron** can be prepared by igniting pure oxide in a current of hydrogen, when the metal remains as a grey spongy mass. It fuses at the highest temperatures producible in a blast-furnace; its fusion, however, can

practically not be effected without its taking up traces, at least, of carbon and silicon. After fusion it is of a white colour, very soft and ductile, and has a sp. gr. of 7·8. At a white heat, iron, long before fusing, becomes soft and sticky, so that it can be 'welded' (a property which it shares with only a very few other metals, *e.g.* platinum). In *dry air* it is not changed; in *moist air* it is slowly oxidized (it 'rusts'). When heated in air it is gradually converted into the oxide Fe_3O_4 (magnetic oxide). At ordinary temperatures iron is not acted on by *pure* water; by water containing air it is slowly oxidized. When heated to redness in a current of steam, it is oxidized into magnetic oxide, hydrogen being formed. Dilute *sulphuric*, also *hydrochloric acid*, dissolves iron, with evolution of hydrogen and formation of ferrous salt ($FeCl_2$, $FeSO_4$). It is not attacked by aqueous alkalies. *Concentrated sulphuric acid*, in the heat, produces ferric sulphate $Fe_2(SO_4)_3$ and sulphurous acid. Dilute nitric acid in the cold dissolves the metal, without gas-evolution; the solution contains *ferrous* and *ammonic nitrates*. $4Fe + 2H_2O + 5N_2O_5 = 4Fe(NO_3)_2 + NH_4.NO_3$.

134. The *commercial varieties* of iron (wrought iron, cast iron, and steel) are essentially alloys of the metal with varying proportions of carbide of iron. Wrought iron contains from 0·0 to 0·6°/₀ of carbon, cast iron from 2 to 6°/₀, and steel from 0·5 to 1·5°/₀. Besides the combined carbon, *grey* cast iron contains a quantity of graphite (carbon) disseminated throughout its mass. Different specimens of cast iron contain varying quantities of silicon and manganese, also traces of sulphur, phosphorus, and arsenic.

Ferrous Salts.

135. The chloride $FeCl_2$ forms white scales, which in absence of air and water melt at a red heat and may be sublimed unchanged at a higher temperature. When heated in hydrogen it is reduced to metal. The hydrated salt

$FeCl_2+4H_2O$ forms bluish-green crystals, easily soluble in water.

136. The sulphate $FeSO_4$ is white. When heated to redness it is decomposed into sulphurous acid, sulphuric anhydride, and ferric oxide. The hydrated salt $FeSO_4+7H_2O$ ('*iron vitriol*') forms bluish green crystals, easily soluble in water, insoluble in alcohol.

137. Reactions of solutions of ferrous salts.—(The solutions are generally bluish green, or, if dilute, colourless.)

Sulphuretted hydrogen, in presence of free mineral acid, produces no change; neutral solutions of the acetate and some other organic ferrous salts are partially precipitated.

Sulphide of ammonium gives a black precipitate of sulphide FeS, insoluble in excess of the reagent, and in ammonia salts generally, insoluble also in ammonia, but easily decomposed and dissolved, by cold dilute hydrochloric or sulphuric acid. The precipitate eagerly takes up oxygen from the atmosphere; it must therefore be washed with water containing some sulphide of ammonium. *Alkalies* (potash, soda, ammonia) precipitate white hydrate, which however soon absorbs oxygen, and thereby assumes first a dirty green and at last a brown colour (hydrated ferric oxide). In presence of ammonia salts the precipitation is not quite complete. If the ammoniacal solution is exposed to the atmosphere, the iron is soon completely precipitated as ferric hydrate.

Ferrocyanide of potassium gives a white precipitate, which in contact with air takes up oxygen and becomes blue, being converted into $(Cy_6Fe)fe_4(fe=\frac{1}{3}Fe=18\frac{2}{3}$ parts of ferricum).

Ferricyanide of potassium gives a blue precipitate, insoluble in hydrochloric acid.

138. Solutions of ferrous salts, when exposed to the air, take up oxygen, and are gradually, but never completely, converted into basic ferric salts, which, from neutral solutions, partially separate out as brown precipitates. Presence of free hydrochloric or sulphuric acid retards, that of alkalies promotes, the oxidation. The magma produced by mixing solutions of ferrous salt and alkali very eagerly absorbs oxygen from the atmosphere. By the action of many oxidizing agents (*e.g.* free chlorine, chloric acid, nitric acid, chromic acid, permanganic acid, etc.), ferrous salts (in aqueous solutions) can be completely converted into ferric ones. The most practical methods are the following:—(1.) Add free hydrochloric or sulphuric acid to the solution, heat, and then add, small quantities at a time, of *chlorate of potash*, or, if the introduction of potassium salts be objectionable, (2.) acidify the solution, heat, add *nitric acid*, and boil for a short time to expel the nitrogen oxides produced. For such quantities as are usually operated upon in analyses, a few drops of nitric acid will, as a rule, suffice.

Ferric Compounds.

139. Ferric oxide Fe_2O_3 may be prepared, (*a.*) by heating ferrous oxalate in contact with air; (*b.*) by heating the nitrate, as long as nitrogen oxides are given off; or (*c.*) by igniting the hydrate. The oxide forms (*a.*) a brown powder, or (*b.* and *c.*) a brown amorphous mass, insoluble in water, difficultly soluble in dilute sulphuric (or nitric) acid, pretty easily soluble, at a gentle heat, in concentrated hydrochloric acid.

140. Ferric chloride Fe_2Cl_6, as prepared by heating iron in a current of dry chlorine, forms black iridescent plates of metallic lustre which, in a current of chlorine, sublime at a temperature somewhat above 100°. The salt is very deliquescent, and easily soluble in water. A very concentrated solution forms a dark brown oily liquid.

141. Hydrated ferric chloride.—An acid solution of ferric chloride (as prepared by heating a solution of the ferrous salt with nitric and hydrochloric acids), when sufficiently concentrated by evaporation, deposits, according to the degree of concentration, either yellow crystals of $Fe_2Cl_6.12H_2O$, or dark red crystals of $Fe_2Cl_6.5H_2O$, both easily soluble in water. A concentrated solution is brown; when diluted with water it becomes yellow. The yellow colour almost completely disappears on addition of large quantities of hydrochloric acid, but reappears, with *great intensity*, on heating.

142. Reactions of solutions of ferric salts.—(The solutions are generally brown or yellow, those of some salts, *e.g.* of 'iron alum,' are colourless. When mixed with a considerable quantity of hydrochloric acid, and heated, they all assume the intense yellow colour of the chloride.)

Sulphuretted hydrogen gives a white milky precipitate of sulphur, the metal remaining in solution as *ferrous salt.* From the *acetate*, a part of the metal is precipitated as sulphide. *Sulphide of ammonium* gives a black precipitate, the solubility relations of which are the same as those of a mixture of ferrous sulphide and sulphur. *Caustic alkalies.*—Solutions of ferric salt, when cautiously mixed in the cold, with potash, soda, or ammonia, become dark brown, but there is no permanent precipitate formed, before a certain quantity of the alkali is added. If a dilute solution to which as much alkali has been added in the cold, as is possible without producing a permanent turbidity be boiled, the whole or most of the iron is precipitated as basic salt.

In case of the acetate, or any other salt mixed with an excess of acetate of sodium (at least 4-5 times '$(C_2H_3O_2)Na$,' for every 1 eqt. of acid radicle in the liquid), the precipitation is quite complete; the precipitate, however, partially re-dissolves on cooling. Excess of *ammonia*, from dilute liquids, precipitates the whole of the iron as brown amorphous hydrate, insoluble in water, in free ammonia, and in ammonia salts. *Caustic potash*, also soda and alkaline carbonates, behave substantially like ammonia, only the precipitate in all cases contains chemically combined alkaline oxide, which cannot be removed by washing. *Ferrocyanide of potassium* gives a precipitate of 'Prussian Blue' ($Cy_6Fe.fe'_4$) (comp. page 86), insoluble in dilute acid. *Ferricyanide* gives no precipitate, but produces a dark brown liquid.

143. *Ferric salts* can be reduced to *ferrous*, by means of *sulphuretted hydrogen*, also by *nascent hydrogen* (zinc and hydrochloric acid)—both reactions go on in the cold—or, in the heat, readily and completely by means of *stannous chloride*, slowly by means of *sulphurous acid.*

144. Blowpipe-tests.—Iron oxides colour the borax bead, in the reducing flame, bottle-green; after oxidation the bead is yellow in the heat, colourless after cooling. Iron compounds, when heated on charcoal with soda, yield an infusible grey powder of metallic iron, which follows the magnet.

Nickel.

145. A silver-white, ductile, and very tenacious metal, attracted by the magnet. Spec. gravity = 8·6 to 9·0. Its melting point lies between those of cast iron and copper. It is not affected by air at ordinary temperatures, and only very slightly at a red heat. *Hydrochloric*, also *dilute sulphuric*, *acid* attacks it slowly; *nitric acid* easily dissolves it. The solutions are green, and contain nickelous salt ($NiCl_2$, $NiSO_4$, $Ni(NO_3)_2$).

146. Nickel oxide NiO, as obtained by igniting the hydrate or carbonate, is a grey powder. The hydrate is green, and is not affected by contact with air. It easily dissolves in dilute acids.

147. *The sesquioxide* Ni_2O_3, formed by the action of *hypochlorite, of soda* on recently precipitated hydrate or carbonate, or by keeping the nitrate at a temperature of about 200°, is a black substance, insoluble in water, scarcely soluble in boiling *acetic acid.* Hydrochloric acid dissolves it, with evolution of chlorine and formation of $NiCl_2$.

148. Behaviour of solutions of Nickel Salts (NiX'_2) to Reagents.

(The solutions are generally green.) *Sulphuretted hydrogen* (in presence of free mineral acid), no precipitate. From a solution of the *acetate*, even in presence of free acetic acid, the metal is slowly, but at last, especially on heating, completely precipitated as sulphide. *Sulphide of ammonium* gives a black precipitate of sulphide NiS, insoluble in water and in ammonia and in ordinary ammonia salts, but slightly soluble in sulphide of ammonium, the more so, the greater the excess of sulphur (the more intense the yellow colour) in the reagent. By addition of a considerable quantity of chloride of ammonium, the solubility of the precipitate in sulphide of ammonium can be diminished, and thus the precipitation be rendered more complete. The sulphide is almost insoluble in *acetic*, and is very slightly attacked by cold dilute (5°/₀) *hydrochloric acid.* *Ammonia* gives a slight green precipitate, soluble in excess of the reagent; the solution is intensely blue. In presence of chloride of ammonium no precipitate is formed. *Potash* (also soda) precipitates (green) hydrate, which is not affected by atmospheric oxygen. *Oxalic acid*, from neutral solution, precipitates gradually the green oxalate $NiC_2O_4 + 4H_2O$. Ammonia easily dissolves this salt; the blue solution when exposed to the air gradually loses its ammonia and deposits green crystals of a double oxalate of nickel and ammonium. If the solution contains an admixture of *cobalt*, this metal accumulates in the mother-liquor. *Nitrite of potassium* and acetic acid, in moderately dilute solutions, give no precipitate. In presence of barium, strontium, or calcium, part of the nickel is precipitated along with one or other of these metals in the form of a yellow crystalline triple-nitrite.

149. Blowpipe tests.—The *borax bead* in the oxidizing flame assumes a *reddish* colour, which is rather intense in the heat, but becomes very much fainter on cooling; if very rich in nickel the bead is dark *brown;* on being fused together with some nitre or other potash salt in the oxidizing flame it becomes *purple.* The *microcosmic salt bead* in the *oxidizing* flame assumes a brown or brownish-yellow colour, which is more intense than that observed in case of borax, but likewise becomes much fainter on cooling. In presence of a *moderate quantity* of cobalt the bead is green. The *borax* bead (but *not* the microcosmic salt one) when heated in the *reducing* flame becomes *grey* from reduced metal, which, on continued blowing, agglomerates and sticks to the wire so as to leave a colourless bead. The reduction succeeds best on charcoal, and can be greatly accelerated by addition of a little *tin.* Nickel compounds, when fused on charcoal in the reducing flame with *carbonate of soda,* yield metallic nickel, as a whitish distinctly metallic-looking *infusible* and perfectly non-volatile powder which follows the magnet.

Cobalt.

150. **Cobalt** in its physical properties, and also in its behaviour to acids, closely resembles nickel. Spec. grav. of compact masses = 8·6.

151. *The oxide* CoO, as obtained by heating the hydrate in absence of oxygen, is greyish green. When heated in air it is converted into another oxide, Co_3O_4. The hydrate of the oxide CoO is a pale red precipitate.

152. *The sesquioxide* Co_2O_3 is obtained in the same manner as, and is similar in its properties to, the corresponding nickel compound. The black oxide, obtained by heating the nitrate to about 200°, is *not* soluble in boiling dilute acetic acid.

153. Behaviour of solutions of Cobalt Salts (CoX'_2) to Reagents.

(The solutions are generally red; that of the chloride becomes blue on heating. A solution containing both nickel and cobalt salt is red, green, or colourless, according to the proportion in which the two metals are associated.)

Sulphuretted hydrogen in presence of free mineral acid, no precipitate. The *acetate* behaves substantially like the nickel salt. *Sulphide of ammonium* gives a black precipitate of sulphide CoS, the solubility relations of which are the same as those of sulphide of nickel, except that it is *not* at all soluble in sulphide of ammonium.

Ammonia precipitates blue basic salt, soluble in excess of the reagent; the solution is brown, but in contact with air, becomes red on standing. In presence of chloride of ammonium the reagent produces no precipitate.

Caustic potash (also soda) gives a precipitate of blue basic salt, which on exposure to air becomes green by oxidation. On boiling, the precipitate is converted into a pale red hydrate $Co(HO)_2$, which however gets generally mixed with some of the brown hydrate of Co_2O_3. *Oxalic acid* produces a pale red precipitate, in which, ultimately, the whole of the metal accumulates. The oxalate is soluble in ammonia, giving a rose-coloured solution, which, on exposure to the air, only *very slowly* deposits the dissolved oxalate. *Nitrite of potassium.*—If a concentrated solution of cobalt salt is mixed with excess of this reagent and enough of acetic acid to produce a strongly acid mixture, the cobalt is slowly but at last completely precipitated. The precipitate is a yellow crystalline powder, the composition of which has not yet been established with certainty. According to Erdmann it is $Co_2O_3.3K_2O.6N_2O_3 + 3H_2O$ (direct result of analysis: $Co_2K_6N_{12}O_x.3H_2O$). In dilute solutions the precipitate appears only after some time, but more readily on stirring. The precipitate ('Fischer's salt'), though insoluble in a solution of acetate of potassium, is perceptibly soluble in cold, and more readily still in hot, water.

154. If a *mixed* solution of cobalt and nickel salt is treated in the way described, the nickel remains dissolved.—(*Stromeyer.*) From the filtrate the nickel is best precipitated by means of carbonate of potash in the heat; the green precipitate (of basic carbonate) is easily washed with hot water.—(*Gibbs.*) To *identify* it as a *nickel* compound, dissolve it in hydrochloric acid, evaporate to dryness, dissolve the chloride in the least quantity of water, and add an excess of dark yellow sulphide of ammonium; a *dark brown* solution of NiS in $(NH_4)_2S.S_x$ will be formed.—(*W. D.*) Or else adopt Plattner's dry-way test (*vide* infra). This method of separating the two metals (by means of NO_2K) is *not* applicable in presence of barium, strontium, or calcium. (See § 148).

155. Blowpipe-tests.—Oxides of cobalt impart to both the borax and the microcosmic salt bead a *blue* colour—in either flame. The colour is so intense that it remains decidedly visible, even in presence of moderate quantities of iron, manganese, or nickel. *Traces* of cobalt produce a violet colour similar to that of the oxidized manganese bead. To detect traces of cobalt in what substantially is a *nickel-borax* bead, fuse the bead on charcoal with a granule of pure *lead* in the reducing flame. The nickel is soon reduced and eliminated by the lead, and the remaining bead, if cobalt is present, exhibits the characteristic blue colour. To detect *nickel* in a substance consisting potentially of the two oxides, dissolve as much as possible of the mixture in a *borax* bead in the oxidizing flame, and then heat the bead on *charcoal* in the *reducing* flame with about 30-50 milligrammes of pure *gold*, taking care to keep the gold well molten, and to let it roll about the flux so as to pick up the particles of reduced metal, until a pure nickel bead would have become colourless. Now detach the gold globule from the flux, and subject it on *charcoal*, in the *oxidizing flame*, to a series of lixiviations with *microcosmic* salt. The first dose of flux generally takes out a small admixture of cobalt, then follows a mixture of the two oxides, and lastly pure nickel oxide, which imparts to the flux the characteristic *yellow* colour.—

(*Plattner.*) (Comp. § 149.) With *soda*, on charcoal, *cobalt* compounds behave like nickel compounds.

156. Nickel and **Cobalt** are distinguished from the other metals of the group by the relative insolubility of their precipitated sulphides in cold dilute (4-5°/₀) hydrochloric acid. If a nickel or cobalt solution is precipitated with a solution of sulphide of *sodium* on *boiling*, the sulphides formed are very compact, can easily be washed out with hot water, and are not at all attacked by *ordinary dilute* (20°/₀) *hydrochloric acid*, so that by means of this acid they can be completely freed from any admixture of sulphides of zinc, iron, etc.—(*Gibbs.*)

Manganese.

157. Metallic manganese has not yet been obtained in the state of purity. The impure metal, as prepared by reducing the oxide with charcoal at an intense white heat, has the appearance of cast iron, but is very soft and brittle. Sp. gr. = 7·1 to 7·2. From moist air it readily absorbs oxygen. Water attacks it slowly, with evolution of hydrogen. Dilute acids, even acetic, easily dissolve it, with evolution of hydrogen and formation of manganous salt ($MnCl_2$, $MnSO_4$, etc.)

158. Oxides of manganese.—The oxide MnO, *manganous oxide*, is a greyish green powder, which, when kept in contact with moist air, takes up oxygen and is slowly converted into a brown hydrate of sesquioxide, Mn_2O_3. *Manganous hydrate* $MnO.H_2O = Mn(HO)_2$ is a white precipitate which eagerly absorbs oxygen from the atmosphere, and is gradually changed into hydrated sesquioxide. Both the oxide and hydrate are easily dissolved by acids, with formation of manganous salts,—'*manganese salts,*' *par excellence.*

Manganic oxide (or sesquioxide) Mn_2O_3 occurs in nature as *Braunite.* The artificially prepared oxide forms a black powder. The hydrated oxide is a brown precipitate. This oxide Mn_2O_3 is the basis of manganic salts. The *Dioxide* MnO_2 (peroxide of manganese) occurs in nature as

Pyrolusite, a mineral which forms black crystals or crystalline masses. The mineral is easily distinguished from other native manganese oxides by its being very soft, and giving a black 'streak' on paper. *All these oxides*, when heated to bright redness in an atmosphere of nitrogen or air, leave brown-red Mn_3O_4; in oxygen, Mn_2O_3; in hydrogen, MnO. The peroxide MnO_2 is insoluble in nitric and in dilute sulphuric acid; when heated with hydrochloric acid it gives manganous chloride $MnCl_2$ and free chlorine; with concentrated sulphuric acid in the heat, it yields, ultimately, manganous sulphate $MnSO_4$ and oxygen. The other oxides, when heated with nitric or hydrochloric acid, or concentrated sulphuric acid, behave like mixtures of peroxide and monoxide.

159. The trioxide MnO_3 is not known in the free state, but only as a constituent of metallic *manganates* ($MnO_3R'_2O$), which are formed by fusing (in a silver dish) any lower oxide of manganese with caustic alkali and nitrate or chlorate of alkali metal. The fused mass contains alkaline manganate (MnO_3R_2O), which imparts to it an *intense bluish green colour*. The fused mass dissolves in water, forming a dark green solution (the colour, however, is less intense than that of the solid substance); if this solution is mixed with a few drops of *alcohol*, and heated, the manganese is completely precipitated as a brown hydrated oxide ($Mn_2O_3.xH_2O$?), the alcohol being oxidized into carbonic and organic acids.

160. Manganic heptoxide Mn_2O_7 ('Permanganic acid').—Solutions of alkaline manganates are stable only in presence of free alkali. If the free alkali is saturated, either directly by addition of dilute nitric acid, or indirectly by passing chlorine into the solution, the latter becomes intensely purple, and now contains *permanganate*, $Mn_2O_7R'_2O$. The reaction in case of nitric acid is $3MnO_3 =$ (hydrated) $MnO_2 + Mn_2O_7$. The action of free chlorine is explained by the following equation: $2MnO_3 + 2K_2O + Cl_2 = 2KCl$

+ $Mn_2O_7.K_2O$. *Alkaline permanganates* dissolve in water, with an intensely *purple* colour, which is visible even after large dilution with water. The colour is not changed by addition of sulphuric or nitric acid, which sets free a part of the permanganic acid, but the acidified liquid is easily decolourized (and the heptoxide in it reduced to manganous salt) by ferrous salt, oxalic acid, sulphurous acid, stannous chloride, and by many other reducing agents.

161. *Manganates and permanganates* when *heated* with hydrochloric or concentrated sulphuric acid behave like mixtures of the respective bases with MnO and active oxygen. Ex. $Mn_2O_7K_2O (= 2MnO.K_2O.O_5) + 16HCl = 2MnCl_2 + 2KCl + 8H_2O + 5Cl_2$.

162. Behaviour of solutions of Manganous Salts to Reagents.

(Pure solutions are colourless, but a very small admixture of manganic salt suffices to impart to them a pink colour.) *Sulphuretted hydrogen.*—No action, not even in the case of acetate. *Sulphide of ammonium* precipitates flesh-coloured sulphide MnS, insoluble in water, and, in presence of an excess of reagent, in ammonia salts. *Yellow* sulphide of ammonium does not precipitate manganese so readily as does the colourless reagent. The colour of the precipitate may be considerably modified by the presence of even very slight admixtures of foreign metals. Sulphide of manganese is easily *dissolved* by *cold dilute mineral acids*, and even by *acetic acid.* The moist *precipitate*, when exposed to the air, eagerly absorbs oxygen, and is gradually converted into *brown* hydrated sesquioxide. Sulphide of manganese, of all the sulphides of the group, is the one which, to solutions of *ammonia salts*, opposes the least degree of stability. A dilute solution of chloride of manganese, when mixed with sal-ammoniac and a sufficiency of *oxalate of ammonia*, on subsequent addition of sulphide of ammonium gives either no precipitate at all, or furnishes one, after some time, which, mainly or entirely, consists of an oxalate.[*] If a mixture of manganous chloride, sulphide of ammonium, and sal-ammoniac is boiled until the volatile sulphide is gone, a considerable portion, at least, of the manganese passes into the solution, from which it can be precipitated—as MnS—by sulphide of ammonium. The undissolved portion of what was originally MnS exhibits a *green* colour. The same green compound (oxysulphide ?) makes its appearance when sulphide of ammonium is added to a hot solution of manganous oxalate in ammonia, or when the flesh-coloured magma formed on addition of sulphide of ammonium to a concentrated solution of $MnCl_2$ is allowed to stand. *Sulphide of potassium or sodium*, from pure solutions of manganous salts, always precipitates flesh-coloured *sulphide*, which does *not* become green on standing.—(Muck; *Zeitschrift für Chemie* for 1869, 580.)

Caustic alkalies give a white precipitate of hydrate which absorbs oxygen from the air, and is thereby gradually converted into brown sesquihydrate. In presence of a sufficiency of *sal-ammoniac*, excess of *ammonia* gives no precipitate, but if the mixture be exposed to the air, it soon becomes turbid, and deposits *brown* sesquihydrate. If, *immediately* after addition of the ammonia, the excess of this reagent is *boiled off*, a colourless solution is formed which is perfectly stable in air. (Separation of manganese from ferricum and aluminium.)

163. *Manganic Salts,*

as a class, are very unstable compounds. The chloride Mn_2Cl_6 can scarcely be said to exist. Of salts derived from oxygen-acids, the phosphate is the only one which dissolves in water without decomposition. In presence of *manganous sulphate*, the sulphate also can remain permanently dissolved. The solutions show the intense *purple* colour of permanganates. All manganic salts when boiled with hydrochloric acid are reduced to manganous compounds, with liberation of chlorine.

164. Blowpipe test.—The *borax bead*, when obtained in the *oxidizing* flame, is violet, when in the *reducing*, colourless.

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[*] The presence of considerable quantities of *citric* or *tartaric acid* entirely prevents the precipitation of *manganese* (but not that of iron, nickel, cobalt, or zinc), by sulphide of ammonium.—(How; *Chem. News*, 19, 137.)

Manganese compounds, when fused with *soda* in the oxidizing flame, give an intensely bluish-green mass containing manganate. When fused with soda on *charcoal*, in the *reducing* flame, they do *not* give metallic manganese, but monoxide which is absolutely non-volatile.

Zinc.

165. Zinc is a bluish-white metal, generally crystalline, and, at ordinary temperatures, brittle. At temperatures between 100° and 150° the metal is ductile, so that it can be drawn out into wire; at 200°, again, it is so brittle as to be easily reducible to powder. Sp. gr. $= 7{\cdot}15$. It fuses at about 400°, and is volatilized at a red heat; it boils at 1040° (*Deville*). At ordinary temperatures it is not much affected by air, but when heated to redness in presence of air, it takes fire and gives off an abundant white smoke of oxide. Boiling *water* attacks the metal slowly; *dilute sulphuric* and *hydrochloric acids* dissolve it readily, with evolution of hydrogen and formation of zinc salts ($ZnCl_2$, $ZnSO_4$). Dilute *nitric acid*, in the cold, dissolves zinc, with evolution of nitrous and nitric oxides; the solution contains nitrates of zinc and *ammonium*. A solution of *caustic potash* (or *soda*) dissolves zinc, with evolution of hydrogen and formation of zincate $ZnO.xR_2O$.

166. The oxide ZnO (the only oxide known) is a light powder, white at ordinary temperatures, yellow in the heat, infusible, and absolutely non-volatile. When heated to dull redness in hydrogen, it is not changed; at a bright red heat it is very slowly reduced to metal. The hydrate is a white precipitate, easily dehydrated by heating. Both the hydrate and oxide (the latter even after exposure to high temperatures) readily dissolve in aqueous acids and alkalies (also in ammonia).

167. Reactions of Solutions of Zinc Salts.

(The solutions are generally colourless.) *Sulphuretted hydrogen*, in presence of a *sufficient quantity* of free mineral *acid, gives no* precipitate. From neutral solutions of mineral salts, a very considerable portion of the metal is precipitated as sulphide: from a solution of the acetate, even if containing free acetic acid, the *whole* of the zinc is thrown down. Any other zinc salt, when mixed with a sufficiency of acetate of soda, behaves to sulphuretted hydrogen like acetate. *Sulphide of ammonium* precipitates the metal completely as *white* sulphide ZnS, which is insoluble in water, in ammonia, and in ammonia-salts,* insoluble also in *acetic acid;* but easily decomposed and dissolved by (even *cold dilute*) *hydrochloric* or *sulphuric* acid. *Ammonia* precipitates white hydrate, soluble in ammonia and in ammonia-salts. *Caustic potash* (also soda) precipitates white hydrate soluble in excess of alkali; the solution, if concentrated, is not changed on boiling; but if dilute, the oxide is reprecipitated. From the alkaline solutions sulphuretted hydrogen completely precipitates the metal as sulphide.

168. Blowpipe tests.—The *borax* bead is colourless. Zinc compounds, when heated on *charcoal* with *soda*, in the reducing flame, give *no* metal, but a strong oxide-ring. The *oxide*, when moistened with *nitrate of cobalt*, and then strongly heated in the oxidizing flame, gives an infusible mass, which, after cooling, exhibits a *pure grass-green* colour. (Comp. § 71.) This is a very characteristic reaction. Sulphide of zinc can, by roasting, be converted into oxide. The green colour comes out quite clearly, even if the sulphide was not perfectly white. Very small quantities of sulphide are best treated in the following manner:—Dissolve in nitric acid, add a trace of cobalt nitrate, evaporate to one drop, take up this drop with a bit of filter-paper, dry and incinerate. The least trace of zinc colours the ash distinctly green. Or else: place some of the precipitate on one end of an asbestos stick, and roast it over a Bunsen lamp. It is soon converted into oxide, which can be recognised by its being yellow in the heat and white upon cooling, and by its becoming green when strongly heated with nitrate of cobalt.

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* ZnS is *not decomposed when* boiled with sal-ammoniac solution.

169. *Uranium* (U = 240)

is a rare element. It occurs in nature chiefly in the form of *pitchblende* (impure U_3O_8). The metal (obtained by the action of sodium on the chloride UCl_4) is similar in appearance to iron, but extremely hard, and endowed with the very high specific gravity of 18·33.

170. Uranous oxide, UO_2, as prepared by ignition of uranic oxalate in hydrogen, forms a black powder, insoluble in dilute hydrochloric and in dilute sulphuric acid, soluble in nitric and in concentrated sulphuric acid. The *hydrated* oxide is easily dissolved by dilute acids, the green solution contains:

171. Uranous salts (Ex. UCl_4). These are easily converted into *uranic salts* by all those reagents which change ferrous into ferric compounds.

172. Uranic oxide UO_3 is a brick-red powder; its hydrate is a yellow precipitate easily dehydrated by heating. The oxide, when kept at a red heat in air, is reduced to U_3O_8, in hydrogen to UO_2. The oxide UO_3 unites with acids to form uranic salts, ⅓d of the oxygen being replaced by its equivalent of acid radicle. Ex. chloride = UO_2Cl_2; nitrate = $UO_2(NO_3)_2$; sulphate $UO_2.SO_4$. In these salts, therefore, the residue (UO_2), not (as in ferric salts, for instance) the metal itself, plays the part of the basic radicle. Uranic oxide unites also with basic oxides; the compounds are called *uranates* (Ex. $Na_2O.2UO_3$).

173. Reactions of Solutions of Uranic Salts. (The solutions are generally yellow.) *Sulphuretted hydrogen* reduces them to uranous salts with precipitation of sulphur. *Sulphide of ammonium* gives a brown precipitate of oxysulphide (UO_2S ?), which, on exposure to air, is soon changed into hydrate with separation of sulphur. The precipitate is easily decomposed and dissolved by dilute acids.

Ammonia gives a yellow precipitate of uranate of ammonia, which is nearly insoluble in water, and perfectly insoluble in ammonia, and in chloride of ammonium. If the precipitate is washed with pure water it goes through the filter; this can be prevented by addition to the wash water of chloride of ammonium. The precipitate is soluble in a solution of *carbonate of ammonia;* the yellow liquid on continued boiling loses its alkaline carbonate, and deposits the whole of the uranium as a yellow precipitate. From the carbonate of ammonia solution, the metal *cannot* be precipitated by *sulphide of ammonium.* *Potash* (soda) precipitates yellow alkaline uranate, insoluble in excess of alkali.

174. Blowpipe tests.—Uranium oxides and *borax* give, in the *reducing* flame a green, in the *oxidizing* flame a yellow, bead.

175. *Thallium*

is a greyish white, soft metal of 11·8 sp. gr. It melts at 294° and is volatilized at a red heat. In contact with air it quickly tarnishes; when heated with a blowpipe flame it gives off a brown smoke of oxide. It does not decompose water, not even on boiling. Dilute sulphuric and hydrochloric acids readily attack it, with evolution of hydrogen and formation of thallious salts ($TlCl$, Tl_2SO_4).

176. Thallious oxide Tl_2O is prepared by exposing the finely divided metal at a gentle heat to air and water. The oxide formed dissolves in boiling water; the solution when evaporated deposits pale yellow needles of hydrate ($TlHO$). The aqueous solution of the hydrate is colourless; it has a strong alkaline reaction, and absorbs carbonic acid from the atmosphere (like a solution of potash or soda). It saturates acids and forms thallious salts.

177. Thallic oxide Tl_2O_3, as formed by burning the metal in oxygen, is a dark brown powder. The hydrate is obtained by precipitating thallic salts with ammonia; it is insoluble in water and in alkalies, but dissolves in acids, forming thallic salts.

178. Solutions of Thallious salts and Reagents. (The solutions are generally colourless.) *Sulphuretted hydrogen*, in presence of free mineral acid, gives no precipitate. *Sulphide of ammonium* precipitates dark brown sulphide Tl_2S, easily decomposed by nitric, but somewhat difficultly soluble in dilute hydrochloric and in dilute sulphuric acid. *Hydrochloric acid* precipitates white chloride $TlCl$, difficultly soluble in water, less soluble still in dilute hydrochloric acid. A concentrated solution of carbonate of soda, in the heat, dissolves large quantities of thallious chloride, of which the greater part separates out again on cooling. *Iodide of potassium* precipitates iodide, which is at first orange, but soon becomes yellow. Iodide of thallium is almost insoluble in water; the presence of moderate quantities of free acid or alkali slightly increases, but that of excess of reagent rather diminishes, its solubility. *Platinic chloride*, from even very dilute solutions, precipitates a pale yellow chloroplatinate $2TlCl.PtCl_4$, soluble at 16°, in about 16,000 parts of water. (Compare chapter on potassium.) *Zinc* precipitates metallic thallium. *Alkalies* give no precipitate.

179. Thallic salts, generally, are decomposed by water, and can exist in solutions only in presence of free acids. From such solutions: *Alkalies* precipitate the whole of the metal as brown gelatinous hydrate. *Hydrochloric acid* gives no precipitate; in presence of thallious salts it precipitates sesquichloride. *Iodide of potassium* on boiling gives a precipitate of thallious iodide beside free iodine. *Sulphuretted hydrogen*, *sulphurous acid*, and other reducing agents, convert thallic into thallious salts.

180. Flame test.—The least trace of a thallium compound, when volatilized in a colourless gas-flame, imparts to it an intense *green* colour. The spectrum of this flame consists of *one* green line. This is the most characteristic and delicate test for the metal.

Summary and Additions.

(*Only* **Aluminium, Chromium, Iron, Nickel, Cobalt, Manganese, Zinc,** *are here taken notice of.*)

181. Behaviour of compact specimens of the metals when heated with the blowpipe on charcoal.—*Zinc* melts readily below redness; when heated to bright redness in the reducing flame, it *boils*, with formation of an abundant *oxide-ring.* In the oxidizing flame it burns with a blue flame. *Aluminium* readily melts at a red heat; it is absolutely non-volatile, and even in the oxidizing flame is scarcely oxidized. *Iron, nickel, cobalt, chromium* are absolutely infusible and non-volatile, and in the oxidizing flame are but slowly oxidized.

182. Behaviour of the Metals to Acids.—*Hydrochloric acid* dissolves them all (zinc, iron, chromium, and manganese very readily; cobalt and nickel only slowly) with evolution of hydrogen and formation of :—

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
$RCl_x =$	$CrCl_2$	Al_2Cl_6	$FeCl_2$	$NiCl_2$	$CoCl_2$	$MnCl_2$	$ZnCl_2$
Solution is	Blue	Colourless	Colourless	Green	Red, if cold Blue, if hot	Colourless	Colourless

If the solutions are treated with *chlorine* in the cold, then (2) and (7) remain unchanged, (1) and (3) are completely, (4), (5), (6) are partially, converted into higher chlorides; if the chlorinated liquids are *boiled*, then the higher chlorides of (4), (5), (6), are reduced again, with evolution of chlorine, and there result solutions of—

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
$RCl_y =$	Cr_2Cl_6	Al_2Cl_6	Fe_2Cl_6	$NiCl_2$	$CoCl_2$	$MnCl_2$	$ZnCl_2$

The colour of (dissolved) chromic chloride Cr_2Cl_6 is violet or green; that of *ferric chloride* is *intensely yellow* in *the heat,* less so in the cold. The chlorides RCl_y are produced at once, if the chlorination is effected by means of hydrochloric acid and *chlorate of potash* in the *heat*. Of the chlorides, RCl_y, ferric chloride is the only one which by the action of *sulphuretted hydrogen* is *reduced*. Products: $FeCl_2$ and sulphur.

183. *Nitric acid* dissolves all the metals named, with formation, in each case, of a nitrate corresponding to the RCl_y (in case of iron and cold dilute acid, *ferrous* nitrate is produced beside *ferric*), and sometimes of nitrate of ammonia. The nitrates, although stable as solutions, are readily decomposed when heated by themselves. If the solutions are evaporated to dryness, and the residues kept at 200° (the heat of a sand-bath) there is left ultimately—

(1)	(2)	(3)	(4)	(5)	(6)	(7)
Cr_2O_3	Al_2O_3	Fe_2O_3	Ni_2O_3	Co_2O_3	MnO_2	ZnO $xZn(NO_3)_2$
Green.	White.	Brown.	Black.	Black.	Black.	White.
Slowly attacked by nitric acid. Insoluble in hot dilute acetic acid.			Easily dissolved by hot nitric acid. Scarcely attacked by hot dilute acetic acid.		Insoluble in nitric and in acetic acid.	Soluble in hot dilute acetic acid.

All soluble in hot concentrated hydrochloric acid [(1) and (2) dissolve *very* slowly, the rest more or less readily] with formation of the chlorides RCl_y.

184. The oxides just named when heated to redness in air yield—

(1) | (2) | (3) | (4) | (5) | (6) | (7)
Cr_2O_3 | Al_2O_3 | Fe_2O_3 | NiO | Co_3O_4 | Mn_3O_4 | ZnO,

and these when heated to redness in hydrogen are reduced to

Cr_2O_3 | Al_2O_3 | ⟵ Metal. ⟶ | MnO | ZnO.[*]

185. Of the several oxides of the metals, *oxide of zinc* is the only one which, when heated on an asbestos stick in the yellow tip of a Bunsen's flame, yields vapour of metal condensible into a '*film*.'

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[*] ZnO at a bright red heat is slowly reduced to metal.

186. When heated in a *reducing* blowpipe flame with *carbonate of soda* on charcoal,

Oxide and salts of *zinc* yield a strong *oxide*-ring, yellow in the heat, white in the cold;

Oxides and salts of *cobalt*, *nickel*, *iron*, yield infusible metal, which, on elutriation of the mass, is obtained as a *powder* following the magnet; but *no* oxide-ring;

Oxides, etc., of *aluminium*, *chromium*, *manganese*, yield neither metal nor oxide-ring.

187. When fused (in a silver dish) with *caustic alkali*, and *alkaline nitrate*, the oxides* of the metals behave as follows. The oxides of—

Manganese	*Chromium*	*Aluminium*
yield MnO_3R_2O. Intensely green, soluble in water; solution green; if heated with alcohol: complete precipitation of the Mn as Mn_2O_3.	yield CrO_3R_2O. Intensely yellow; soluble in water; solution intensely yellow; not reduced by alcohol.	yield $Al_2O_33R_2O$. White; soluble in water; solution colourless; if heated with excess of *sal-ammoniac*: complete precipitation of the alumina as hydrate. Sulphide of ammonium acts like chloride, but is not so safe a precipitant.

The oxides of *iron*, *nickel*, *cobalt*, are *not* converted into soluble alkali-salts; oxide of zinc (probably) partially passes into soluble zincate. (*Vide* infra.) Upon these reactions is founded the most exact method for testing a mixture of oxides, carbonates, chlorides, etc., of the iron group, for *chromium*, *manganese*, and *aluminium*.

188. The *oxides*, when heated on charcoal with *nitrate of cobalt* in the oxidizing flame, behave as follows:—

Oxide of zinc yields a *green* mass.*

Oxide of aluminium a blue mass.*

The rest give no characteristic colourations.

189. *The salts of the metals* may be divided into two classes, viz.: I. those which are formed by the union of some strongly basic oxide (such as K_2O, Na_2O) with one or another of the following oxides: Cr_2O_3, CrO_3, Al_2O_3, ZnO, MnO_3, Mn_2O_7; and II. those which are formed by the union of decided acids (hydrochloric, nitric, sulphuric, etc.), with the oxides: Cr_2O_3, Al_2O_3, Fe_2O_3, FeO, NiO, CoO, MnO, ZnO. [The bases Ni_2O_3, Co_2O_3, Mn_2O_3, CrO, are of little practical importance, and therefore are here left out of consideration.] Those of the

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* These tests are available, of course, not only for the oxides, but also for those salts of the respective metals which, under the circumstances of the experiments, are, or by some operation or other—*e.g.*, mere heating, roasting, etc.,—can be converted into oxides.

190. *Salts of Class I.*

in which *potash or soda* plays the part of base (provided they contain a sufficiency of basic oxide) are soluble in water, and consequently the corresponding hydrated oxides dissolve in aqueous potash or soda, in the cold at least. The solutions exhibit the following properties:—

ZnO.	Al_2O_3.	Cr_2O_3.	CrO_3.	MnO_3.	Mn_2O_7.
Colourless.		Green.	Yellow.	Green.	Purple.
Not precipitated on boiling		On boiling, the whole of the Cr_2O_3 is precipitated.	Not precipitated on boiling.		
if *concentrated.*	whether dilute or strong.				
If the solutions are heated with some alcohol, then—					
Solutions remain unchanged.				The whole of the metal is precipitated (as a hydrated oxide).	
If solutions are heated with excess of sal-ammoniac, then—					
Oxide remains dissolved.	The whole of the oxide is precipitated.		No change.		

Note.—The oxide ZnO, even after ignition, is readily soluble in ammonia; the hydrates of Cr_2O_3 and Al_2O_3 are slightly soluble in ammonia, but, from these solutions, can be completely precipitated by boiling off the ammonia.

191. The oxide MnO_3 is stable in strongly alkaline solutions only; if the solution is acidified, the oxide is decomposed, with formation of a precipitate of peroxide and a solution of heptoxide. *Acid* solutions of the oxides CrO_3 and Mn_2O_7 are reduced by *sulphuretted hydrogen* to salts of Cr_2O_3 and MnO respectively, with precipitation of sulphur.

192. *Salts of Class II.*

Solutions of the oxides ZnO, MnO, CoO, NiO, FeO, Cr_2O_3, Al_2O_3 in excess of aqueous *mineral acid*, are not affected by *sulphuretted hydrogen.* But if, previous to the application of this reagent, the solution, in each case, was mixed with a sufficiency of *acetate of soda*, then the effect is as follows:—

Zinc: readily precipitated in the *cold* as *white* sulphide.

Cobalt, *Nickel:* slowly precipitated in the cold, but more readily on heating, as *black* sulphide.

Manganese: chromium, *aluminium:* not changed.

By the joint effect on *neutral solutions* of any of the salts II, of *sulphuretted hydrogen* and enough of *ammonia* to keep the mixture neutral to the end, or of *sulphide of ammonium*, the metal in each case is completely precipitated. The properties of the precipitates are given in the following table (193)—

Cr_2O_3-	Al_2O_3-	FeO-	MnO-	ZnO-	NiO-	CoO-(Salt).
$Cr_2O_3xH_2O$.	$Al_2O_3xH_2O$.	FeS.	MnS.	ZnS.	NiS.	CoS.
Green.	Colourless; semi-transparent.	Black.	Light coloured; but becomes brown on exposure to air.	White, not discoloured in air.	Black.	Black.
Readily dissolved by cold dilute hydrochloric acid; products					Scarcely attacked by cold 10 % hydrochloric acid.	
Cr_2Cl_6	Al_2Cl_6	$FeCl_2$	$MnCl_2$	$ZnCl_2$		
And water.		And *sulphuretted hydrogen.*				
					Slightly soluble in yellow sulphide of ammonium. Solution brown.	
All the precipitates are readily dissolved in the heat by hydrochloric acid on addition of *chlorate of potash* or nitric acid; products						
Cr_2Cl_6	Al_2Cl_6	Fe_2Cl_6	$MnCl_2$	$ZnCl_2$	$NiCl_2$	$CoCl_2$

194. Supposing each of these solutions to be largely *diluted* with water, to be *neutralized*, in the cold, with carbonate of soda, and then—

(*a.*) *boiled with excess of acetate of soda, then—*

Cr_2O_3-	Al_2O_3-	Fe_2O_3-	MnO-	ZnO-	NiO-	CoO-(Salt).
Greater part of the metal remains dissolved.	The *whole* of the metal is *precipitated* as basic salt, which on cooling, partly redissolves.		Solutions, in presence of a sufficiency of free acetic acid, remain clear.			

195. *If* (*b.*) *the* **cold** *solutions be treated with carbonate of barium, then—*

The whole of the metal is (after some time) precipitated as basic salt.			The whole of the metal remains dissolved.			A *small* quantity of metal is precipitated; the greater part (in general) remains dissolved.

196. *If* (*c.*) *the* (*acid*) *solutions be mixed with sal-ammoniac and excess of ammonia, then—*

The metal is precipitated as basic salt; and if the excess of ammonia be boiled off, the precipitation is *complete.*			The metal remains dissolved. On exposure to air—			
			The metal is gradually precipitated as hydrated Mn_2O_3. If excess of NH^3 be boiled off (at once) the metal remains permanently dissolved.	No change.	Substantially no change.	Change from red to brown, but no precipitate.

197. Behaviour to **caustic potash or soda** of solutions of salts of

Ferrosum, *ferricum*, *cobalt*, *nickel*, *manganese*,	Precipitate of hydrate, insoluble in excess of reagent.

Aluminium, *chromium*, *zinc*, } Precipitate, soluble, in the cold at least, in excess of alkali.

(Compare § 190.)

Upon these reactions exact methods of separation *cannot*, in general, be founded. Thus for instance, from a mixed solution of ferric and chromic salt, caustic potash precipitates not only the iron, but also part or the whole of the chromium. A mixed solution of chromic and zinc salts, when mixed with excess of alkali, gives a permanent precipitate, which may contain the whole of both metals. *Ferricum* and *aluminium cannot* be completely separated by addition of even a large excess of concentrated alkali in the heat; a more exact method for effecting this separation is, first, by means of sulphuretted hydrogen, to reduce the ferric to ferrous salt, then to add excess of alkali and to boil, until the ferrous hydrate is converted into black anhydrous oxide ($Fe_3O_4 + xFeO$) and at last—after dilution—to filter. The precipitate is almost free from alumina.—(*Fresenius.*)

Examination of a Solution of Salts for Metals of the Iron Group.

198. Supposing, from a given solution of metallic salts, say, for fixing ideas, nitrates, we had first precipitated the silver, mercurosum, and part of the lead by means of hydrochloric acid; the filtrate had then been evaporated with hydrochloric acid, to expel the nitric acid, and from the solution of chlorides thus obtained we had then, after dilution with water, etc. (see §§ 39, 46, 77), eliminated the copper and arsenic groups by means of sulphuretted hydrogen, as sulphides, and filtered these off. From such filtrate the whole of the iron group can be precipitated by means of *sulphide of ammonium*, and thus be separated at least from any potassium or sodium that may be present; but whether or not the barium group metals and the magnesium remain dissolved, mainly depends on the nature of the acids present.

199. If (*a*) the solution contained none other but such acids, of which the Ba, Sr, Ca, Mg salts are soluble in water and in ammoniacal salts, then, substantially and generally at least, the barium group and the magnesium remain dissolved. To effect as complete a separation as possible, and at the same time to render the precipitate filterable, add a somewhat considerable quantity of sal-ammoniac; take care, if nickel should be present, to use *colourless* sulphide of ammonium; keep the mixture for some time at a gentle heat (40°-50°), shake violently and filter. If these precautions are observed, the filtration will, as a rule, proceed satisfactorily, and generally the bulk at least of what does not belong to the iron group remain dissolved. But whatever we may do, if the precipitate is bulky, it will carry down traces at least of the oxides BaO, SrO, CaO, MgO; and if the one last named is present along with *alumina*, a part or the whole of it will go down as aluminate. The method just given for the separation of the iron and barium groups becomes quite inapplicable, if

200. (*b.*) The solution contains certain acids (of which *phosphoric* and *oxalic* may be named as being the most important). In presence of these, part of the barium group and of the magnesium are sure to be, and the whole of them may be, precipitated along with the iron group, in the form of such salts as phosphate of lime, phosphate of ammonia and magnesia, oxalate of lime, etc.

Seeing then that the *precipitate* produced in the filtrate from the copper and arsenic groups, by *sulphide of ammonium* may possibly have a very complex composition, we readily perceive that it would be absurd, in all cases, at once to apply to such a precipitate a complete and general method of separation, devised on the supposition of the most general case. It evidently is much better first to apply, to separate portions of the liquid, a series of preliminary tests to prove, if possible, the absence of certain groups of the complex of metals potentially present, and, on the basis of the data furnished by these tests, to devise a method of analysis which, by the shortest possible route, will lead to the detection of those metals, the presence or absence of which is not yet definitively established. Regarding the way in which this pioneering investigation should be conducted it is not easy to lay down definite rules. Beginners may provisionally adopt the following method:—

201. Given: the filtrate from the sulphuretted hydrogen precipitate—which we will suppose to have been freed, as it ought to have been, previous to the application of sulphuretted hydrogen, from nitric and other *oxidizing acids.*

(1.) Observe its colour, compare it with that of the original solution, and interpret your results according to §§ 169-174, 182, 191. (See also § 287.)

(2.) Test a small portion with ammonia and sulphide of ammonium, and draw what conclusions you can from the colour of the precipitate—if there is one—and its behaviour on addition to the mixture of dilute hydrochloric acid in the cold. (§ 193.)

(3.) From a somewhat larger portion boil off the sulphuretted hydrogen, add excess of *carbonate of soda,* and boil; the precipitate will contain all that is present of iron group and barium group metals. Collect it on a filter, wash with hot water, and test separate portions.

(*a.*) For *zinc* by applying Bunsen's film-test. (Comp. (§§ 185, 104.)

(*b.*) With *borax* before the blowpipe. Cobalt, if present, will give a blue bead, even if diffused throughout a considerable mass of foreign matter.

(*c.*) For manganese, chromium, aluminium, by the process suggested in § 187.

(*d.*) For *barium, strontium,* by mixing some of the precipitate with a drop of hydrochloric acid, exposing the mixture on one end of a fine platinum wire to the heat of a Bunsen's flame, and noting the flame colour. (Comp. Ex. 7 and Div. IV. on flame tests.)

(4.) To another portion, add some drops of *nitric acid* and boil down. A *yellow* colour indicates *iron.* After sufficient concentration, test for barium, strontium, and calcium, by adding a few drops of sulphuric acid and about one-third of the volume of the whole of alcohol, and, if necessary, allowing to stand for one or two hours. A precipitate by the acid alone indicates barium, strontium; if it only appeared after addition of alcohol: calcium. A part of the liquid, if iron is not obviously present, may serve to test for *sesquioxides* as a class, by means of *sal-ammoniac* and *ammonia.* (§ 196.)

Note.—Negative results obtained in the test for Co and Ni in (2) or in tests (3) *a*, *b*, and *d*, must not be considered as final.

The results of these tests will sometimes amount virtually to a complete analysis of the iron group precipitate, but even if they do, they are all the better to be confirmed by a *systematic analysis.*

202. We will now, for the sake of generality, assume the preliminary tests had *not* brought out much beyond showing that we had to deal with a comparatively complex case, and on the basis of this supposition lay down a scheme of exhaustive analysis. For fixing ideas, let us suppose the group (cobalt, nickel) to be pretty largely represented. In this case it is expedient, first of all, to eliminate at least the bulk of this group. We accordingly begin by precipitating the liquid—after saturation of the free acid by means of ammonia and addition of a somewhat considerable quantity of *sal-ammoniac*—with an excess of *sulphide of ammonium.* (Regarding the *modus operandi*, see Exercise 32 (2) and

Note i. page 116.) The *filtrate* (Note ii. page 116) contains all the *potassium* and *sodium*, and *generally*, a part at least of the *barium*, *strontium*, *calcium*, and *magnesium*. The precipitate is washed, first, with very dilute lukewarm sulphide of ammonium, then with hot water, and lastly, digested, *in the cold* and in *absence of air*, with 5°/₀ *hydrochloric acid*, whereby it is split up, substantially at least, into:

A Black Residue and	**A Filtrate**
consisting of NiS and CoS. How these two metals can be separated from each other, was shown in § 154. Regarding the potentially present foreign admixtures, see Note 3, page 116.	which can contain only traces of nickel or cobalt, but contains all that was present in the original precipitate of Fe, Mn, Zn, Al, Cr, Ba, Sr, Ca, Mg, and of the acid radicles PO_4''', C_2O_4'', etc.

To analyse the filtrate,

peroxidize the iron by heating the liquid with a granule of chlorate of potash, add *sal-ammoniac* (if necessary), and after cooling, and with continuous agitation, *ammonia*, drop by drop, until the mixture is alkaline; then boil, until the vapours no longer smell of ammonia. At last filter, and wash the precipitate with hot water.

Precipitate.	**Filtrate.**
A = hydrates of Al_2O_3, Cr_2O_3, Fe_2O_3. B = BaO, SrO, CaO, MgO as phosphates, ammonio-phosphates, oxalates, etc. C = traces of (Ni, Co, Mn, Zn) O.	D = Mn, Zn (traces of Ni and Co) as ammonia-double-salts, also part at least of that portion of the (Ba, Sr, Ca, Mg) O = 'E' which was originally 'carried down' by the alumina, etc.

203. *To analyse the* precipitate,

i.e. the complex A+B+C, employ, of the following two methods, the one which applies to the case.

1. **Barium group absent.**—Fuse with *caustic soda* and nitre in a silver dish, treat the fused mass with water, remove the manganese (present as MnO_3R_2O) from the solution by

heating it with a few drops of alcohol; dilute and filter. The **filtrate** contains all the Cr, Al, P, and part perhaps of the Zn, as alkaline

Chromate (*yellow*).
Aluminate (*colourless*).
Phosphate (*colourless*).
Zincate (*colourless*).
(Compare § 187.)

To test for Al_2O_3 and P_2O_5, add excess of *sal-ammoniac* and heat until all the free ammonia is driven off, then filter.

Precipitate.	**Filtrate.**
(1.) $Al_2O_3.P_2O_5$. (2.) $Al_2O_3.xH_2O$.	(In absence of (2.), possibly) alkaline phosphate and (in any case) the zincate, which can be detected by means of $(NH_4)_2S$.

Regarding the detection of the phosphoric acid in (1) and in the filtrate, see Div. III.

That portion of the fused mass which did *not* dissolve in water, together with the Mn_2O_3 precipitated by the alcohol, may contain:—Fe_2O_3, Mn_2O_3, MgO, (Ni, Co, Zn)O, possibly also traces of (Ba, Sr, Ca), as phosphates, or even as oxides. (See note 4, page 116.)

II. **Barium Group present.**—Dissolve the precipitate (A+B+C) in the least quantity of hydrochloric acid, add sulphuric acid, to precipitate the Ba and Sr, and then about $\frac{1}{3}$ of the volume of the whole of alcohol, to precipitate the Ca. After some hours' standing, filter off the sulphates and wash them with dilute alcohol. (See note 5, page 116.) From the filtrate expel the alcohol by evaporation and reprecipitate by means of sal-ammoniac and ammonia (*vide* supra). The **precipitate** is, potentially, a mixture of hydrated Cr_2O_3, hydrate or phosphate of Al_2O_3 and Fe_2O_3, and PO_4MgNH_4, which may be analysed according to method I., page 112.

The **filtrate** contains, potentially, alkaline *oxalates* and *phosphates* and *magnesia*, and may besides contain traces of Ni, Co, Mn, Zn.

204. *Analysis of complex $D+E$ (filtrate from A, B, C).*

From this filtrate, supposing it to contain tolerable quantities of *zinc*, the bulk of this metal can be precipitated, as ZnS, by means of *sulphuretted hydrogen in the cold*, when the rest of the metals remain dissolved along with a trace of zinc, which, after addition of a few drops of *acetate of ammonia*, can be precipitated (free from Ni and Co) by cautious addition of H_2S water. From the filtrate the *manganese* is precipitated (together with the Ni and Co) by means of *ammonia* and H_2S, and identified with the blowpipe. The Ba, Sr, Ca, and Mg remain dissolved. (Comp. note 6, p. 116.)

205. If the group (*cobalt*, *nickel*), according to the preliminary tests, is seemingly *absent*, then—in absence of Ba, Sr, Ca—it is better, in the filtrate from the *sulphuretted hydrogen* precipitate, to *peroxidize* the *iron*, and then at once to precipitate the complex A, B, C (the sesquioxides, etc.), by means of sal-ammoniac and ammonia, and from the filtrate to precipitate what is present in the shape of Mn, Zn (Ni, Co), by means of *sulphide* of *ammonium*. If, in this case, the *barium group* is present, it may, of course, *previous* to the application of the sal-ammoniac and ammonia process, be eliminated by means of *sulphuric acid* and *alcohol*. To insure as successful a separation as possible, the iron should first be peroxidized (because ferrous sulphate is far less soluble in dilute alcohol than ferric) and the liquid be concentrated by evaporation, before the sulphuric acid is added.

206. In absence of chromium

The method detailed above had better be replaced by the following one:—

(Supposing alumina, iron, and possibly phosphates or oxalates of Ba, Sr, Ca, Mg to be present.) Peroxidize the iron, allow to *cool*, dilute largely with water, add, drop by drop, solution of carbonate of soda, until the precipitate, locally formed, is very slow in re-dissolving, then add an excess of solid *acetate of soda.* If the liquid does not assume the *red colour* characteristic of *ferric acetate,* this proves that there is more phosphoric acid present than can be precipitated by the iron and Al_2O_3, as $R_2O_3.P_2O_5$. In this case add *ferric chloride* until the liquid *is* strongly coloured by ferric acetate. Now boil and filter in the heat.

The precipitate

contains all the *iron*, alumina, and *phosphoric acid,* and the whole of what is virtually present of *oxalate of lime,* possibly also barium and strontium as oxalates. If necessary, test a portion of the precipitate for Ba, Sr, Ca, by dissolving it in hydrochloric acid, and adding sulphuric acid and alcohol. To search for *alumina,* add to the hydrochloric solution, or to the filtrate from the sulphates after expulsion of the alcohol, caustic soda in excess, filter, and from the filtrate precipitate the *alumina* (as such, or as phosphate) by means of *sal-ammoniac.* The *precipitate* produced by the caustic alkali may contain traces of nickel and cobalt —and invariably contains part at least of the alumina. The separation of Fe and Al is more complete if, previous to the addition of the caustic soda, the ferric salt was reduced to ferrous by means of H^2S. (Comp. § 197 and note 7, page 117.)

The filtrate

in absence of $C_2O_4H_2$ contains all the *protoxides* MeO. To precipitate the

Zinc, add, in the cold, sulphuretted hydrogen water, until there is either an excess of this reagent, or until a dark-coloured precipitate (NiS or CoS) begins to make its appearance. Filter rapidly, and from the

Filtrate precipitate the nickel and cobalt by neutralizing the free acid with caustic soda, and then saturating the liquid in the heat with sulphuretted hydrogen. To redissolve the manganese which may have gone down as MnS, add excess of acetic acid, digest for some time and filter.

The *filtrate* contains the *manganese* beside Ba, Sr, Ca, Mg (K, Na) salt. From this liquid the *manganese* is best precipitated (as MnO_2) by adding *bromine*-water (or liquid bromine) and digesting for some time at about 80° C. The rest of the metals remain dissolved.

The *alkali metals,* on account of the introduction of large quantities of sodium salts, must be searched for in a separate portion of the filtrate from the copper and arsenic group precipitate.

NOTES.

207. 1. This precipitate is generally very difficult to filter. If the mixture, previous to the filtration, is boiled until the excess of sulphide of ammonium is expelled, the precipitate becomes more manageable, but, at the same time, some of the manganese and iron at least is re-dissolved. The best method probably would be, first to boil off the excess of $(NH_4)^2S$, then to add again enough of this reagent to re-precipitate what has gone into solution of the iron group, to keep the mixture in a stoppered beaker flask until the precipitate has settled completely, to draw off the clear liquor, and while this liquor was being examined, to wash the precipitate, once by decantation with warm highly diluted sulphide of ammonium, and then, on the filter, with hot water.

2. If the filtrate should be brown from *sulphide of nickel*, this metal can be removed by first boiling off the greater part of the sulphide of ammonium, and then removing the rest of the sulphur by cautious addition of *mercuric chloride*. The precipitate contains the whole of the nickel as sulphide, beside sulphide or chlorosulphide of mercury. The two metals can be easily separated by igniting the precipitate (in a draught place, on account of the poisonous mercury vapours), or in other ways.

3. Any lead or cadmium, etc., which escaped precipitation by sulphuretted hydrogen, will find their way into this precipitate. [So would, in case of *thallium*, that part of the metal which had not gone down along with the silver, etc., as chloride.] The lead and cadmium, after conversion of the whole into a slightly acid solution of chlorides, are easily removed by means of sulphuretted hydrogen. [The *thallium*, after conversion of the sulphides into nitrates, may be eliminated by means of *iodide* of *potassium*.]

4. This precipitate can be analysed by dissolving it in hydrochloric acid and then applying the method described in § 206.

5. The *sulphate precipitate* not unfrequently contains *magnesia* and metals of the *iron group*. To recover these, wash it with hot water and precipitate from the filtrate what is present of Mn, Zn, etc., with sulphide of ammonium. The filtrate must be tested for *calcium* and *magnesium* according to §§ 228 and 238.

6. A more exact method for the examination of this filtrate is the following: first, evaporate to dryness and burn off the ammonia salts at the lowest possible temperature. Then dissolve the residue in the least quantity of acid (NO_3H or HCl), precipitate the metals as carbonates, by means of carbonate of soda in the heat, convert the carbonates into *nitrates*, and heat these in a porcelain basin in a sand-bath

to about 200°, until they are decomposed as completely as possible at that temperature. Now, to extract the

Zinc, boil with dilute *acetic acid*, and filter. From the filtrate the zinc is precipitated by sulphuretted hydrogen. The filtrate from the ZnS contains the Ba, Sr, Ca, Mg, associated usually with part of the nickel.

After elimination of the zinc, treat the washed residue with hot nitric acid to dissolve the *nickel* and *cobalt*. The *manganese* remains as MnO^2.

7. To separate even small quantities of *cobalt* or *nickel* from *iron*, convert the metals into a slightly acid solution of chlorides (which must contain the iron as Fe_2Cl_6), dilute to about 500 times the weight of the iron with water, and add to the *cold* liquid, drop by drop, a solution of *carbonate of ammonia*, until the mixture is opalescent, without being actually turbid, and remains so on being left to itself. This being done, boil for some time and filter. The iron (also the alumina if present) is completely precipitated; the nickel and cobalt pass into the filtrate, from which they can be precipitated by means of sulphide of ammonium. If this method (or the acetate of soda process) is applied to a liquid which contains only Al_2O_3 but no Fe_2O_3, it is as well to add some ferric chloride to enable one to hit upon the exact point of neutrality.

208. If the method given in §§ 202-205 was applied to a liquid containing one or some of the rarer elements of the group, then the *uranium*, *titanium*, and the rare *earths* would have to be looked for in the *sesquioxide* (A, B, C) precipitate; of the earths, however, some might pass into the ammoniacal filtrate. The *uranium* can be extracted by digestion with a solution of *carbonate* of *ammonia*. (Comp. § 173.) The *titanium*, from the hydrochloric solution of the precipitate, may be precipitated by long continued boiling, as TiO^2. In the fusion process it would probably ultimately pass into solution along with the alumina, etc. (Comp. § 128 *et seqq.*) Regarding the *earths*, it is difficult to make any short statement worth having. The *thallium* would go (mainly at least) with the *nickel* and *cobalt* sulphides. (See Note 3, page 116; also § 175 *et seqq.*)

D. BARIUM GROUP.

BARIUM, STRONTIUM, CALCIUM.

209. The metals are pale-yellow solids, endowed with metallic lustre and a certain degree of ductility. When heated in absence of air they melt at a red heat, but even at somewhat higher temperatures remain unvolatilized.

The specific gravities of Ba, Sr, Ca, are (about 4), 2·54, and 1·58 respectively. When exposed to the air they rapidly tarnish, and are gradually converted into hydrates and carbonates. When *heated* in air they burn, with a brilliant light, into oxides $R''O$. They readily decompose *water* at ordinary temperatures, with formation of hydrate and hydrogen. Towards dilute acids they behave like the metals of the iron group; only their actions are far more violent.

210. The oxides (baryta, BaO; strontia, SrO; lime, CaO) are white or greyish-white solids, which, when heated on charcoal with the blowpipe-flame, do not fuse, but emit an *intense light;* they are absolutely non-volatile, even at the highest temperatures producible by an *oxyhydrogen* blowpipe. They act energetically on *water*, with formation of hydrates $R''O.H_2O{=}R''(OH)_2$.

211. These **hydrates**, when heated to redness, behave differently. *Barium* hydrate melts, but is not otherwise changed. *Strontium* and *calcium* hydrates lose their water ($Ca(HO)_2$ the more readily), and are reduced to oxides.

The hydrates are all three soluble in water, but to different extents. Solutions, saturated in the heat, of the *barium* or *strontium* compound, deposit, on cooling, abundant crops of crystals of the composition $R''(HO)_2.8H_2O$. [Baryta crystals dissolve in about 20 parts, the strontia ones in 50 parts of cold water.] A solution saturated in the cold, of *calcium hydrate* ('lime water,' which contains about $\frac{1}{700}$th of its weight of CaO), when heated to ebullition, deposits a part of its dissolved hydrate. The solutions exhibit a strongly alkaline reaction to litmus and turmeric paper; they readily saturate all properly so-called *acids* with formation of salts, of which the *normal* ones are *neutral*, or, if derived from '*weak*' acids, such as acetic, for instance, *alkaline* to litmus. The *hydrate-solutions* eagerly absorb *carbonic acid* with formation of precipitates of *carbonates* $ROCO_2$, which are slightly soluble in *carbonic acid* water, from which solutions they are re-precipitated on boiling.

Strontia or *lime*, when heated in *oxygen*, remain unchanged, *baryta* (*i.e.* the oxide BaO), under these circumstances, is converted, partially, into

212. **Peroxide of barium** BaO_2—a greyish-white solid, which, when *strongly* ignited, or heated in *steam*, loses one half of its oxygen, and is reduced to BaO or $Ba(OH)_2$ respectively. The *peroxide*, when added gradually to an *excess* of *cold*, *dilute mineral acid*, is decomposed into baryta-salt and a solution of *peroxide of hydrogen* H_2O_2.

The following tables give synoptic views of the properties and certain reactions of the most important **salts** of the group, and also, for the sake of comparison, of the corresponding compounds of **magnesium.**

213.—I. *The Chlorides.*

	Barium.	**Strontium.**	**Calcium.**	**Magnesium.**
Dry chlorides $R''Cl^2$; properties, solubilities in water and in aqueous hydrochloric acid.	White sodids fusible at a red heat into colourless liquids, which, in *absence of water*, remain undecomposed. They are all easily soluble in water; the			
	Ba-salt is almost insoluble in strong *hydrochloric* acid.	*Sr-salt* also is *less soluble*, in presence than in absence of HCl.	*Ca- and Mg-salts* are easily soluble in aqueous hydrochloric acid.	
Dry chlorides and alcohol.	Insoluble in *absolute*, slightly soluble in ordinary (86%) alcohol.	Dissolves in 116 parts of cold absolute and in less of ordinary alcohol.	Easily soluble in even *absolute* alcohol.	
Formulæ of salts, crystallized from water.	$BaCl_2.2H_2O$, stable in moist air.	$SrCl_2.6H_2O$ deliquescent, soluble in 6 parts of ordinary alcohol.	$CaCl_2.6H_2O$, deliquescent.	$MgCl_2.6H_2O$, deliquescent.
On dehydration by heating.	The Ba- and Sr-salts remain undecomposed.		The *Ca-salt* is very slightly decomposed.	The *Mg-salt* is largely decomposed, with formation of insoluble basic salt.

214.—II. *The Nitrates* $R''ON_2O_5$

are white salts, which, when heated, for themselves, are decomposed, leaving, ultimately, residues of oxide $R''O$. They are all soluble in water; from the solutions they can be obtained in crystals.

(*Nitrates of*)

	Baryta.	**Strontia.**	**Lime.**	**Magnesia.**
Dry salts and *alcohol.*	*Insoluble* in *absolute*, slightly soluble in ordinary *alcohol.*		Soluble in even absolute alcohol.	
Salts crystallized from water. Formulæ and properties.	$Ba(NO_3)_2$. Soluble in 12·5 parts of water of 15°; less in dilute nitric acid, insoluble in the strong acid.	(1.) $Sr(NO_3)_2$ octahedra. (2.) $Sr(NO_3)_2 . 4H_2O$ monoclinic. (1.) dissolves in 5 parts of cold water.	$Ca(NO_3)_2 . 4H_2O$. Deliquescent.	$Mg(NO_3)_2 . 6H_2O$. Deliquescent; soluble in 9 parts of alcohol of 0·840, less so in absolute alcohol.
On cautious *dehydration* by *heating*	These three nitrates remain undecomposed.			$Mg(NO_3)_2$ is partly decomposed.

215.—III. *The Carbonates.*

The carbonates $R''OCO_2$ occur in nature; $BaCO_3$ as *Witherite;* $SrCO_3$ as *Strontianite;* $CaCO_3$ as *limestone, marble,* etc. ('Iceland spar' is pure crystallized $CaCO_3$); $MgCO_3$ as *Magnesite.* The carbonates $BaCO_3$, $SrCO_3$, $CaCO_3$ are obtained by decomposing the solutions of the chlorides or nitrates with *alkaline carbonates,* in the form of white precipitates, which, if formed in the heat, are granular, and sometimes distinctly crystalline. The carbonate

$MgCO_3$ cannot be thus formed: the precipitate formed in magnesia-salt solutions by addition of carbonate of potash or soda, is a basic salt, $MgO.xCO_2.yH_2O$ of variable composition. *All these carbonates* are easily decomposed and dissolved by dilute hydrochloric, nitric, acetic acid. The *precipitates* (Ba, Sr, Ca) CO_3, taking them in the granular form which they assume if formed in the heat, are only very slightly soluble in cold or hot water. The presence of carbonate of ammonia ($(NH_4)_2CO_3$) diminishes, that of sal-ammoniac increases, their solubility; when boiled for a sufficient time with a solution of the latter reagent, they are, to a very *large extent*, decomposed and dissolved as chlorides. (A precipitate of carbonate or hydrate of magnesium is very readily dissolved by boiling sal-ammoniac solution.) The precipitated carbonates—

	$BaCO_3$	$SrCO_3$	$CaCO_3$	Mg-carbonates
Require for solution, of (1) *pure water*,	(1) 15,000 prts.	18,000 prts.	10,000 prts.	
(2) of water containing *caustic* NH_3 and *carbonate* of, NH_4	(2) 140,000 ,,	57,000 ,,	(?)	See § 237.

The recently formed precipitates, when digested with solutions of *alkaline sulphates*, behave as follows:—

$BaCO_3$ is readily and completely converted into $BaSO_4$, especially on boiling.	$SrCO_3$ and $CaCO_3$ are not changed, not even on boiling.

The carbonates, when kept for a sufficient time at sufficiently high temperatures, are reduced to oxides. In the case of the *magnesia* carbonates, the temperature required lies below visible redness. With the *calcium* salt the decomposition commences, but cannot be completed at a dull red heat, at which temperature the *strontium* and barium salt remain unchanged. Quantities of one gramme or less, if heated within a platinum crucible (of about 15 cc. capacity) over a gas blowpipe, behave as follows:—

$BaCO^3$ remains (absolutely ?) unchanged.	$SrCO_3$* is as good as completely reduced after about twenty minutes.	$CaCO_3$† is more easily reduced than the Sr-salt.

216.—IV. *The Sulphates*

exist in nature; $BaSO_4$ as *heavy spar;* $SrSO_4$ as *cœlestine;* $CaSO_4$ as *anhydrite;* $CaSO_4.2H_2O$ as *gypsum;* $MgSO_4.H_2O$ as *kieserite* (in Stassfurth). Ordinary *sulphate of magnesia* $MgSO_4.7H_2O$ is easily soluble in water; moderately dilute solutions give *no* precipitate on addition of $\frac{1}{3}$ to $\frac{1}{2}$ of their volume of *alcohol.* The precipitates formed on addition of *sulphuric acid* to solutions of salts of *barium, strontium, calcium,* are $BaSO_4$, $SrSO_4$, $CaSO_4.2H_2O$ respectively. These precipitates are more or less sparingly soluble in water (*vide* infra), but they are all three absolutely insoluble in alcohol, and as good as insoluble in moderately dilute alcohol, even in presence of moderate quantities of *free mineral acid.* The calcium salt loses its water at a temperature far below redness. The anhydrous sulphates stand the strongest red heat without decomposition, but when kept at this temperature along with *charcoal,* are reduced to sulphides RS. By fusion with about ten times their equivalent of *alkaline carbonate* they are readily converted into carbonates. They can be distinguished from one another by the properties given in the following table—

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* W. D.

† *Small* admixtures of Sr or Ba-salt in the lime salt, are readily caustized along with the latter.—(*Engelbach.*)

<table>
<tr><th>$BaSO_4$</th><th>$SrSO_4$</th><th>$CaSO_4.2H_2O$</th></tr>
<tr><td>The precipitate, if produced in the cold, is, at first, milky, and runs through the filter. On continued boiling, especially in presence of free acid, it becomes granular and filterable.</td><td colspan="2">The precipitates are, at first, pasty and very voluminous[*] (consist of a hydrate of $SrSO^4$ and a higher hydrate of $CaSO_4$ respectively?); but on standing after some time, and on boiling at once, become crystalline. They never show any tendency to pass through the filter.</td></tr>
<tr><td colspan="3"><i>The granular precipitate is soluble:—</i></td></tr>
<tr><td>in about 400,000 parts of pure <i>water</i>.</td><td>in 7000 parts of cold and in 10,000 parts of boiling water.</td><td>at 35° in 390 times the weight of the anhydrous sulphate of water; at 100° in about 460 parts.</td></tr>
<tr><td colspan="3">The presence of free HCl or HNO_3 <i>increases</i>, that of <i>H_2SO_4 diminishes</i>, the solubilities of the precipitates. In boiling 20°/₀ <i>hydrochloric acid</i> they dissolve,</td></tr>
<tr><td>The Ba-salt in about 2000 parts.[†]</td><td>The Sr-salt in about 200 parts.[†]</td><td>The Ca-salt very readily.</td></tr>
<tr><td colspan="3"><i>If the precipitates are digested in the cold, for about</i> 12 <i>hours, with excess of a concentrated solution of carbonate of ammonia, then</i>[‡] <i>the</i></td></tr>
<tr><td>$BaSO_4$ remains unchanged.[§]</td><td colspan="2">Sr- and the Ca-salt are completely converted into <i>carbonates.</i></td></tr>
<tr><td colspan="3">The same effects are produced by ¼ hour's boiling with a mixed solution of 1 part of carbonate and 3 parts of sulphate of potash.[‡]</td></tr>
</table>

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[*] A solution containing as little as 1 part of $SrCl^2$ in 100, when mixed with excess of dilute sulphuric acid, soon assumes the form of a paste, so that the test-tube can be turned upside down without a drop running out.

[†] W. D.

[‡] According to *H. Rose.*

[§] Substantially, not absolutely.—(*Fresenius.*)

<table>
<tr><th>$BaSO_4$</th><th>$SrSO_4$</th><th>$CaSO_4$</th></tr>
<tr><td colspan="3"><i>The precipitates when digested for some hours in a close flask at</i> 100°, <i>with twice their equivalents of a solution, in</i> 20-30 <i>parts of water, of neutral</i> oxalate of ammonia, <i>and some drops of caustic ammonia, behave as follows</i>[*]<i>:—</i></td></tr>
<tr><td>$BaSO_4$ remains absolutely unchanged.</td><td>$SrSO_4$ is very largely, and by one repetition of the process can be almost completely, converted into oxalate.[†]</td><td>$CaSO_4$ is completely converted into oxalate.</td></tr>
<tr><td colspan="3">The addition to the mixture of once or twice $(NH_4)_2SO_4$, for every $(NH_4)_2C_2O_4$, does not alter the effects, except that, in the case of $SrSO_4$ the decomposition never goes to the end. But if, instead of ammoniacal water, 12 % <i>acetic acid</i> be used as a medium of the action of excess of $\{2\ (NH_4)_2SO_4 + 1\ (NH_4)_2C_2O_4\}$, then—</td></tr>
<tr><td>$BaSO_4$ remains unchanged.</td><td>$SrSO_4$ remains, substantially at least, undecomposed.</td><td>$CaSO_4$ is completely converted into oxalate.</td></tr>
</table>

Behaviour of aqueous solutions of Barium, Strontium, and Calcium Salts to Reagents.

217. *Sulphuretted hydrogen*, *sulphide of ammonium*, *pure ammonia*, produce no change. *Caustic potash*[‡] liberates hydrate, of which a part *may* separate out as a precipitate. The precipitates are amorphous and bulky; those produced in *barium* or strontium salt *dissolve* completely, the *calcium* one *increases*, on heating. (Comp. § 211.) Hydrate of *lime* being quite *insoluble* in a *dilute* solution of *caustic potash*,[§] this

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[*] W. D.

[†] On repeated treatment of $SrSO_4$ with $(NH_4)_2C_2O_4$, a point is soon arrived at, when another dose of reagent no longer extracts any SO_4; but the washed precipitate, when treated with dilute acid, always leaves a small residue of undecomposed $SrSO_4$.

[‡] The reagent should be absolutely free from carbonate and sulphate.

[§] Upon this fact is founded the customary method for the preparation of caustic potash from carbonate.

reagent may serve to completely precipitate that base from solutions of its salts. *Carbonate of ammonia*, even in presence of *sal-ammoniac*, gives a precipitate of carbonate. The precipitation is more complete in the heat than in the cold.

218. *Oxalate of ammonia* gives a white powdery precipitate of oxalate. The *lime* salt is practically insoluble in *water*, in *ammonia*, and in ammonia salts, and almost insoluble in, even hot, dilute *acetic acid.* The *baryta* salt dissolves in 2600 parts of water, more readily in sal-ammoniac, and still more so in *acetic acid.* The *strontium* salt dissolves in 12,000 parts of water, and, also regarding its behaviour to the other menstrua named, is intermediate between the other two.

219. *Dilute sulphuric acid.* From *barium-salt* solutions the metal is completely precipitated, even in presence of moderate quantities of free hydrochloric or nitric acid. In moderately dilute solutions of *strontium* salts, an immediate precipitate of $SrSO_4$ is produced; the precipitation is promoted by heating. In very dilute solutions the precipitate, if at all, appears only after some time; in presence of a sufficient quantity of free hydrochloric or nitric acid no precipitate is formed. From concentrated solutions of *calcium* salts, a part of the metal is precipitated as $CaSO_4\,2H_2O$; dilute solutions remain clear. But in all cases, even in presence of considerable quantities of free acid, a practically complete precipitation of the metal can be effected by addition, to the mixture, of a sufficiency of alcohol. (This holds *a fortiori* for *barium* and *strontium.*)

219. a. An *aqueous* solution, saturated in the heat, of *sulphate of barium* is (practically) pure water; a similar solution of the *strontium* salt gives a faint precipitate with *alcohol*, and a very perceptible one with chloride of *barium*, but remains clear on addition of *oxalate* of *ammonia.* A solution of sulphate of *lime* gives strong precipitates with *alcohol*, with *barium salts*, and with *oxalate of ammonia.*

A solution, saturated in the heat, of *oxalate* of *calcium* in dilute (10%) acetic acid is practically free from this metal; a solution obtained in the same way from oxalate of *strontium* gives a *faint* precipitate, the corresponding solution of the *barium* salt gives a strong precipitate on addition of *sulphuric acid* and heating.*

220. **Hydrofluosilicic acid** ($SiF_4.2HF$), in solutions of *baryta-salts*, gives a colourless crystalline precipitate of $BaSiF_6$, which is perceptibly soluble in water and in dilute mineral acids, but—even in presence of moderate quantities of free acid—almost insoluble in *alcohol.* *Strontium* and *calcium* salts are *not* precipitated, not even on addition of alcohol.

221. **Bichromate of potash,** when applied to neutral or moderately acid solutions of the *acetates*, is, like hydrofluosilicic acid, a specific and tolerably sensitive precipitant for *barium* (precipitate $BaCrO_4$).

222. **Arsenious acid.**—An aqueous solution of this reagent, when added to a solution of *chloride of calcium* along with some ammonia, gives a white precipitate of arsenite of lime, difficultly soluble in water, but soluble in large quantities of ammonia salts, especially in the arsenite. Baryta salts gives a slight precipitate after twenty-four hours' standing. Strontia salts are not at all precipitated.

222. a. **Phosphate of soda** gives a white precipitate, soluble in acids, including acetic.

Dry-way Tests.

223. When a small quantity of a *barium*, *strontium*, or *calcium* salt is exposed, on a hair-fine platinum wire, to the flame of a Bunsen's lamp, or to a *blowpipe* flame, it generally imparts to the flame a colour which, in each case, is characteristic of the *metal.*

The *barium* flame is intensely yellowish-green.
„ *strontium* „ crimson.
„ *calcium* „ is yellowish-red.

When the flames are viewed through the *spectroscope*, each metal is found to yield a peculiar spectrum,* different from those of the other two. By means of the spectroscope, the least quantities of *barium* or *strontium*, and (though less satisfactorily) also of *calcium*, can be identified with certainty. The flame colours and spectra come out best with the *chlorides*. In the case of *barium* or *strontium*, the carbonates and sulphates also give sufficiently intense colours; the corresponding salts of *calcium* however had better first be converted into chlorides, which, with the sulphate, is easily effected by first reducing it to sulphide in the reducing blowpipe flame and then moistening the product with hydrochloric acid. Certain non-volatile salts will give flame-colours only, after having been moistened with hydrochloric acid. *Silicates* must first, by fusion with alkaline carbonates and treatment of the mass with water, be converted into *carbonates*. When a mixture of the three sulphates is exposed to a flame, then, generally at least, the *barium* colour comes out first and after some time is succeeded by the one characteristic of strontium.

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* W. D.

224. The sulphates of *strontia* and *baryta*, when mixed with carbonate of soda and heated in a *reducing flame* on charcoal, furnish *transparent* beads, which on continued blowing at last are *completely sucked in* by the charcoal. *Sulphate of lime* under these circumstances yields a *turbid* bead, of which only that part which consists of sulphide and carbonate of sodium creeps into the charcoal, while the calcium (sulphide + carbonate) remains as an infusible mass, which, on being strongly heated, emits an intense light. By means of this test, an admixture of lime salt in cœlestin or heavy spar can be detected with great facility.—(*Plattner.*)

Examination of a solution of salts for Barium, Strontium, and Calcium.

Given a solution of metallic salts which is free, or by the application of sulphuretted hydrogen in presence of free acid has been freed, from the copper and arsenic groups, and it is clear (after what was said in § 198 and in the preceding §§ of this chapter) that, in *presence of substances precipitable by ammonia and sulphide of ammonium*, the only straightforward method for the separation of the *barium group* from the rest of the metals is, *previous* to the application of these reagents, to precipitate it out in the form of *sulphate*. This may be done in two ways. After having concentrated the liquid by evaporation to about 100 times the weight of (Ba, Sr, Ca), presumably present, one way is,

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* The spectra are probably those of the *oxides*, not of the metals themselves.

225. First to precipitate with excess of *sulphuric acid* in the *heat*, whereby the whole of the *barium*, and substantially also the *strontium*, are eliminated as sulphates (precipitate A), and then, from the filtrate, after cooling, to precipitate the *calcium* by addition of a quantity of alcohol which is such that, while sufficient for the purpose, it does *not* cause any noteworthy quantity of *magnesia* or of protoxides of the iron group to separate out. These foreign sulphates, if they should make their appearance, are easily distinguished from the lime salt by their forming comparatively large crystals. Iron, if present in quantity, should, previous to the application of the alcohol, be peroxidized by means of nitric acid.* With a little practice, the proper quantity of alcohol is easily hit upon. From one third to one half of the volume of the mixture is generally sufficient to cause a practically complete precipitation of the lime on 2–3 hours' standing. Instead of eliminating the lime as a separate precipitate ('B'), we are, of course, at liberty to

226. Separate it out jointly with the baryta and strontia (precipitate='A+B'). In either case the precipitate must be washed with dilute alcohol. The filtrate, before it can be examined for the iron, magnesium, and potassium groups, must be freed from *alcohol* by evaporation.

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* The sesquioxides (Al_2O_3, Cr_2O_3, Fe_2O_3) are not likely to be precipitated by moderate quantities of alcohol, unless associated with a sufficiency of alkaline (*i.e.* K or NH_4) sulphate, in which case they may go down as '*alums*.'

227. The method just detailed for the separation of the barium group is the best that can be chosen, if the examination for its three members is the only thing aimed at. If, however, a complete analysis be contemplated, then to have to delay the examination for the iron group until after the precipitation of the lime, and the presence in the liquid of large quantities of alcohol and sulphuric acid, are great inconveniences, and it is generally better to begin by removing from the solution what can be precipitated, by means of ammonia and *sulphide of ammonium*, when, in general, a part of the *barium group* and of the *magnesium* are precipitated, along with the iron group (as phosphates, oxalates, aluminates, etc.), while the rest passes into the filtrate ('F'). From the hydrochloric acid extract of the sulphide of ammonium precipitate the metals Ba, Sr, Ca, Mg can be eliminated: the magnesium as part of a solution free from foreign metals except potassium or sodium, the other three as sulphates, as shown in §§ 203 *et seq.* From the filtrate F the barium group is best precipitated by means of *carbonate of ammonia* in the heat (precipitate = 'C'), when, in presence of a sufficiency of ammonia salts, the bulk at least of the *magnesium* remains dissolved. If large quantities of ammonia salts should have accumulated in the liquid, appreciable quantities of barium, strontium, and calcium escape precipitation. Hence, if carbonate of ammonia gives no precipitate, it is as well to test separately, for barium with sulphuric acid, and for calcium with oxalate of ammonia. But it is far better in such a case, and even necessary, if the highest degree of exactitude is aimed at, to remove the ammonia salts by evaporation and ignition, and, to the hydrochloric solution of the fixed residue, to apply the sulphuric acid method. Let us now see how the several products which may result from the application of these methods can be analysed or identified.

228. Precipitate (**A** + **B** = [SO_4(Ba, Sr, Ca) + traces of sulphates of Mg, Ni, etc.] To examine this precipitate, first wash it with small successive portions of hot water, remove from the filtrate what is present of iron group metals by means of sulphide of ammonium, and test for *calcium* with oxalate of *ammonia.** By long-continued washing the whole of the calcium might be removed; but this is a tedious process, which, moreover, entails the loss of a considerable portion of the strontium. It is better, therefore, to stop the washing process as soon as the foreign sulphates are removed (and the presence or absence of calcium established), and to apply to the residue

229. *Rose's method of analysis, i.e.* by digesting the precipitate for 24 hours in a cold concentrated solution of *carbonate of ammonia,* to convert the strontium and calcium into *carbonates,* and after having washed the precipitate (now $BaSO_4 + x(Sr,Ca)CO_3$) with cold water, to extract these two metals by means of dilute *nitric acid.* The sulphate of *baryta* remains undissolved, and is easily identified by means of the flame test; the two nitrates, after evaporation to dryness (which must be completed within a flask at about 110° in a current of air), can be completely separated by means of cold *absolute alcohol,* which dissolves the *calcium salt* only. (Comp. §§ 214 and 216.)

Precipitate B (impure $CaSO_4$).—The right way of identifying the calcium in this precipitate follows at once from what was said regarding 'A+B.'

230. *Precipitate A* ($BaSO_4 + xSrSO_4 +$perhaps a trace of $CaSO_4$). This precipitate must be washed with small successive portions of hot water, so as to remove the mother liquor without dissolving more than is unavoidable of the strontia salt. If the wash-waters, even after removal of the free acid, continue to be precipitated by alcohol and by chloride of barium, this indicates the probable presence of strontium. If the last wash-waters remain clear on addition of barium salt, the precipitate probably consists, substantially, of sulphate of barium. An approximate separation of the two sulphates may be effected by treating the precipitate with about 200 times its weight of boiling *hydrochloric acid* of 1·1 sp. gr. The strontium accumulates in the solution, in which, after evaporation to dryness, it can, even in presence of moderate quantities of barium, be identified by means of the spectrum apparatus. The *barium* accumulates in the residue, and, although large quantities of strontium salt may have remained, can be detected by the green colour it imparts to a Bunsen's flame. In case of need we can fall back upon Rose's process, which, according to whether the barium or the strontium were found apparently absent, must be applied to the undissolved residue or to the residue from the hydrochloric solution.

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* The filtrate from the CaC^2O^4 may contain Mg.

231. *Precipitate C* (carbonates of Ba, Sr, Ca, and possibly Mg).—These carbonates can, of course, easily be converted into salts of any other acid; we have therefore here the choice among a great number of analytical methods. We may, for instance, dissolve the precipitate in dilute hydrochloric acid, and, after precipitation of the *barium* and *strontium* with sulphuric acid in the heat, examine the filtrate for *calcium* by saturation of the free acid with ammonia and addition of oxalate of ammonia. The magnesia, if present, remains dissolved. The oxalate, if it appears only in the form of a faint turbidity, may possibly consist of strontium salt. To test it for calcium, collect it on a filter, incinerate, dissolve the ash in a few drops of hydrochloric acid, precipitate with sulphuric acid in the heat (precipitate $SrSO_4$), and test the filtrate for lime with ammonia and oxalate of ammonia. A *large* precipitate is sure to consist substantially of lime salt. To test it for traces of *strontium*, ignite it in a small platinum crucible over a gas blowpipe, boil the residue ($CaO+xSrO$) with water and filter. The filtrate contains the strontium and some of the calcium. The two metals, after conversion into dry nitrates, can be separated by means of absolute alcohol. Another method is to convert the metals into a solution of *acetates*, and to precipitate the *barium* either by means of *bichromate of potash* (as $BaCrO_4$), or by addition of *hydrofluosilicic acid* and alcohol (as $BaSiF_6$). In either case the precipitation, if we give it sufficient time, is practically complete, while the strontium and calcium pass into the filtrate, from which, in the first case, they may be precipitated successively by means of *sulphuric acid* and by ammonia and *carbonate of ammonia* respectively, while, in the second, they can be precipitated jointly by means of *sulphuric acid* and additional alcohol.

231a. Whichever of the methods above described we may adopt, we must always remember that they are all imperfect, and consequently not forget to identify each of the products as a compound of the metal it is supposed to contain. Traces of any of the three metals when mixed up with comparatively much of one or both of the other two may escape any of the methods given, and in exact analyses must, if necessary, be specially searched for. To detect traces of *barium* or *strontium* in what is substantially a *calcium* compound, convert the metals into carbonates or oxalates, and these, by ignition, into oxides. This being done, the *baryta* and *strontia* can be extracted and approximately separated from lime, by means of hot water.—(*Engelbach.*) To detect traces of *baryta* in what is substantially oxalate of *lime* or *strontia*, boil the precipitate with 10°/₀ *acetic acid*, filter, and precipitate with *sulphuric acid*. The precipitate (by theory $BaSO_4$) will be free from lime salt, but may contain strontia. The best method for the extraction from a 'sulphate of baryta' precipitate of traces of *strontia*, *probably* is, to convert the *strontia*, by digestion of the precipitate in ammoniacal *oxalate of ammonia*, into oxalate (according to § 216), and from the washed precipitate to extract this salt by means of dilute hydrochloric acid.

E. MAGNESIUM GROUP.*

MAGNESIUM (LITHIUM).

Magnesium.

232. **The metal.**—Magnesium is a silver white, soft, and pretty ductile metal of 1·74 specific gravity. It melts and volatilizes at about the same temperatures as zinc. It is not affected at ordinary temperatures by dry air; in moist air it gets covered with a film of oxide. When heated to redness in air it burns with an intense white light and formation of an abundant white smoke of oxide. A thin strip of metal, when once kindled, continues burning by itself. On water and dilute acids it acts like zinc, but more violently.

233. **The oxide** MgO ('Magnesia') is a light white powder, absolutely infusible and non-volatile even at the highest temperatures. It is *not* reduced when heated in hydrogen, or on charcoal in a reducing blowpipe flame. When moistened with *cobalt solution*, and then heated in the oxidizing flame on charcoal, it forms a *red* infusible mass. It readily dissolves in *hydrochloric* and in dilute *sulphuric acid;* the solutions contain $MgCl_2$ and $MgSO_4$ respectively. It is soluble also on continued boiling, in *sal-ammoniac* solution.

234. **The chloride** $MgCl_2.6H_2O$ forms colourless deliquescent crystals, which are very readily soluble in water and in absolute alcohol. When the aqueous solution is concentrated by evaporation beyond a certain point, the salt is partially decomposed, with elimination of hydrochloric acid and formation of an insoluble oxychloride. By repeated evaporation the salt can be almost completely decomposed. By repeated ignition with *carbonate of ammonia* it is converted, ultimately, into oxide.

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* Beryllium, which for purely practical reasons was enumerated among the iron group metals, is far more similar, in its general character, to magnesium. Lithium, so to say, forms the link between magnesium and the alkali metals.

235. The nitrate (comp. § 214) when kept at 200° is converted into a basic salt, which is soluble in hot dilute *acetic acid*, and can be dissolved also by digestion in a solution of nitrate of ammonia. When ignited, it leaves oxide.

236. The sulphate $MgSO_4.7H_2O$ forms colourless crystals which are soluble in less than their own weight of cold water; insoluble in absolute, but moderately soluble in dilute, alcohol. Six out of the $7H_2O$'s go off at 150°, the seventh can be driven out at a dull red heat, without decomposing the sulphate itself. When repeatedly ignited with sal-ammoniac it is converted into a mixture of oxide and oxychloride.

237. Behaviour of Solutions of Magnesia Salts to Reagents.

Sulphuretted hydrogen, sulphide of ammonium: no visible change. *Caustic potash* (also *soda, baryta*) precipitates the metal almost completely as hydrate, a white precipitate, very slightly soluble in water, but easily dissolved, even in the cold, by *sal-ammoniac* and other ammonia salts.

Ammonia precipitates a part of the metal as hydrate; in presence of a sufficiency of ammonia salt no precipitate is formed even on boiling. If the *ammoniacal solution* is mixed with one of *alkaline phosphate*,* the magnesium is gradually, but—in presence of a sufficiency of free ammonia—at last completely precipitated in the form of a crystalline double phosphate $PO_4Mg(NH_4)6H_2O$. In dilute solutions the precipitate appears only after some time, but more readily on stirring. While slightly soluble in water, it is practically *insoluble in dilute ammonia*, but a little more soluble in a mixture of *sal-ammoniac* and *ammonia*. Dilute acids, including acetic, easily dissolve it. This, *in absence of the barium group* and of *heavy metals*, is a characteristic and very sensitive test for magnesia. *Sesquicarbonate of*

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* Microcosmic salt is said by some chemists to work best.

ammonia gives no precipitate in the cold; on heating, a part of the metal is precipitated as basic carbonate. In presence of a sufficiency of *sal-ammoniac*, *no* precipitate is formed. When, however, an excess of a *concentrated* solution of the carbonate $(NH_4)_2CO_3$ (*in practice*, a mixture of sesquicarbonate and free ammonia) is added to a concentrated solution of magnesia salt, the magnesia is, after some time, *almost completely* precipitated in the form of the crystalline salt $MgCO_3(NH_4)_2CO_3 + 4H_2O$, which, though slightly soluble in water and in ammonia salts, is almost insoluble in a strong solution of carbonate of ammonia $(NH_4)_2CO_3$. *Oxalate of ammonia*, when added to moderately dilute solutions, gives, after some time, a crystalline precipitate of a double oxalate of magnesia and ammonia; in presence of a sufficiency of *sal-ammoniac*, however, the liquid remains clear. *Dilute sulphuric acid*, even in presence of moderate quantities of alcohol, gives *no precipitate*. Nor does *hydrofluosilicic acid*.

Magnesium salts do not, as such, impart any *colour* to a non-luminous gas-flame.

Detection of Magnesium.

238. In an *aqueous* salt-solution which is free of, or has been freed from, the metals of the copper, arsenic, iron, and barium groups, *magnesia* is easily detected (after supersaturation of the free acid, if present, by ammonia) by means of *phosphate of soda*. A small precipitate, however, must not be assumed to be the double phosphate, PO_4MgNH_4, unless it is, or on standing becomes, distinctly crystalline. If flocculent, it may entirely consist of phosphate of *alumina*, which oxide is not unfrequently present in consequence of its slight solubility in ammonia.

239. *Lithium* ($Li' = 7$)

occurs in nature as an essential constituent of certain rare minerals—for instance, of *petalite*, *spodumene* (both essentially silicates of alumina and lithia, in which the lithia is partially replaced by potash and soda), *triphylline* (a phosphate of ferrous, manganous, and lithic oxides), *lepidolite* (lithia-mica). *Traces* of lithium are frequently found to accompany potassium and sodium in ordinary minerals, mineral waters, the ashes of certain plants, etc.

240. The metal has the colour of silver, and is very ductile. It is the lightest of known metals, possessing the low specific gravity of 0·589. When exposed to the air it readily tarnishes, but not by any means so rapidly as sodium or potassium. When strongly heated in air it burns with a brilliant white light into a mixture of oxide Li_2O with some of a peroxide. It readily decomposes *water* in the cold, but less violently than potassium and sodium do. Dilute acids dissolve it with evolution of hydrogen and formation of lithia salts, *e.g.* LiCl.

241. The oxide Li_2O can scarcely be said to be known. Its *hydrate* LiHO is a white solid, similar in many respects to caustic soda, but far less soluble in water. Its solution is strongly alkaline and readily saturates all acids. The hydrate fuses at a temperature below redness, but even at a white heat does not apparently volatilize. Lithia readily absorbs *carbonic acid* with formation of the

242. Carbonate Li_2CO_3, a white crystalline salt, soluble in about 80 parts of water at any temperature (*Troost*), but far more soluble in sal-ammoniac solution. The acid carbonate $LiHCO_3$ does not appear to exist, but the neutral salt, like the carbonates of the barium group, dissolves, more readily than in pure water, in water kept saturated with *carbonic acid;* from such solution it separates out, on evaporation, in small crystalline scales; small admixtures of potash or soda remain dissolved. The dry carbonate fuses at a dull red heat, but at the same time loses a part of its carbonic acid; at a bright red heat a very considerable portion of the CO_2 goes off, but no lithia is volatilized. Fused carbonate of lithia was formerly supposed to attack platinum, but according to *Troost* this is the case only if the salt is contaminated with rubidium or cæsium.

243. The chloride LiCl—when crystallized from water below 10°, $LiCl.2H_2O$—is a deliquescent salt, very readily soluble in water. Even if anhydrous, it easily dissolves in absolute alcohol and also in a mixture of this liquid and ether (chlorides of potassium and sodium are insoluble in the latter menstruum). The aqueous solution when evaporated to dryness is only very slightly decomposed.

The nitrate ($LiNO_3$; at temperatures below 10° it crystallizes with $2\frac{1}{2}H_2O$) is a very deliquescent salt.

244. The sulphate ($Li_2SO_4.H_2O$ dissolves in about 3 parts of cold water and in about 3·4 parts of water of 100°. It is not to the same extent 'insoluble' in alcohol as the corresponding sodium or potassium salt.—$LiHSO_4$ does not exist.

245. The phosphate Li_3PO_4 is the least soluble of all lithium salts, requiring 2500 parts of pure water and 3900 parts of dilute ammonia for solution. The presence of ammonia-salt increases its solubility. Solutions of lithium salts, when evaporated with phosphate of soda and enough of caustic soda to keep the liquid alkaline, yield a precipitate of the phosphate Li_3PO_4.

The **bitartrate, chloroplatinate, perchlorate**, are easily soluble in water.

246. Reactions of salt-solutions.—To sulphuretted hydrogen, sulphide of ammonium, carbonate or oxalate of ammonia in presence of sal-ammoniac,—lithia salts behave like magnesia salts. They differ from these in this, that their base (Li_2O) *cannot* be eliminated by *boiling* with excess of baryta-water, or milk of lime.

247. Flame test.—The least quantity of a lithium salt, when volatilized in a colourless gas flame, imparts to it a *crimson* colour. In presence of *sodium*, the colour does not appear. *Small* quantities of potassium do not interfere with the test; large quantities do. The *phosphate* colours the flame only if previously moistened with hydrochloric acid. To apply this test to *silicates*, they must first be decomposed by means of concentrated sulphuric acid or by fusion with sulphate of lime, or—if these reagents do not answer the purpose—by means of *hydrofluoric acid.*

The spectrum of the lithium flame is highly characteristic; it consists mainly of *one* very bright *red* line situated between the red potassium and the yellow sodium line. This line is distinctly visible, even if the quantity of lithium in the flame is too minute to produce a distinct colour, and it is *not* eclipsed by those of potassium or sodium.

F. POTASSIUM GROUP.

SODIUM, POTASSIUM (RUBIDIUM, CÆSIUM).

248. The metals* have the colour and lustre of silver. At and below certain very low temperatures they are hard and brittle, but at ordinary temperatures they are soft like wax, and very ductile. They are all *lighter* than water, and melt at temperatures below 100° C. They are all volatile, and at temperatures below 1040° (the boiling point of zinc) enter into ebullition. But at far lower temperatures

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* What is stated in this paragraph is derived from observations on potassium, rubidium, and sodium only; cæsium has not as yet been obtained in the metallic state.

(for instance, when heated in a combustion-tube with a Bunsen's lamp) they give out vapours, which in the case of potassium exhibit a green, in the case of rubidium a blue, in the case of sodium *no* colour. The metals when kept in *perfectly dry air* remain unchanged, but when exposed to ordinary *moist* air, quickly tarnish, with formation of a crust of hydrate and carbonate. When strongly heated in air, they burn with a brilliant light into oxide R_2O and peroxide $R_2O.O_x$. They decompose *water* with great violence, even at the lowest temperatures, yielding solutions of hydrate RHO. A piece of potassium or rubidium, when thrown on water, at once takes fire, or rather sets fire to hydrogen evolved, which burns along with more or less of metallic vapour, and the flame consequently exhibits a violet colour. (Comp. § 260.) *Potassium*, *sodium* (and probably also the two other alkali metals), readily act on *alcohol*, with formation of solutions of *ethylates* RC_2H_5O, which compounds in absence of air and water possess great stability even at high temperatures. Water decomposes them, with formation of RHO and $C_2H_5.OH$.

The metals readily unite with *mercury*, forming amalgams, which in the case of sodium, at least, are solid, even if they contain only a small percentage of alkali metal.

249. The following table gives some of the chemico-physical constants of the four metals:—

Name.	Sodium.	Potassium.	Rubidium.	Cæsium.
Atomic weight,	Na = 23	K = 39	Rb = 85·4	Cs = 133
Spec. Gravity,	0·972	0·865	1·52	(?)
Fusing point,	95.°6	62°.5	38°.5	Below 38°5*
Boiling point 'T,'	* About 1040	Less than Tna	* Less than Tk	* Less than Tr

250. In their general chemical character the four metals are very closely allied to one another: it is however to be observed that potassium, rubidium, and cæsium resemble one another far more than they do sodium. Generally speaking, an alkali metal is the more easily fusible, the more volatile, the more electropositive, and its oxide the stronger a base, the higher its atomic weight.

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* Probably.

251. The oxides R_2O are little known. Their *hydrates* (the '*caustic alkalies*'), RHO, are white non-transparent solids, which, when exposed to a dull red heat, melt into colourless oily liquids, and at certain considerably higher temperatures are volatilized without apparent decomposition. The fused hydrates readily dissolve *glass* and most other *silicates*, and attack all *metals* except *gold and silver* (and iron?). They are extremely soluble in water: *caustic soda* dissolves in 1·7 parts of water at 18°, the rest are still more soluble. The solutions are strongly 'caustic' (*i.e.* they readily attack and dissolve animal tissues, including the epidermis of the skin). The hydrates are soluble also in *alcohol*. [The corresponding carbonates and sulphates are insoluble, the chlorides difficultly soluble in this menstruum; hence caustic alkalies, which are contaminated with these salts, may be purified by solution in alcohol.] The *alkalies* are the strongest of known bases; they readily unite with, and completely saturate, all acids; and their solutions, even if largely diluted with water, colour red litmus paper blue, and yellow turmeric paper brown. The solid hydrates when exposed to the air, eagerly absorb water and deliquesce into solutions, which, in their turn, absorb *carbonic acid;* this, in the case of *soda*, leads to the ultimate re-solidification of the deliquesced mass.

252. The peroxides.—*Sodium* and *potassium* when heated, first in *dry air* and then in *dry oxygen*, are converted into *dioxides* R_2O_2. In the case of potassium, the *dioxide*, on treatment with more oxygen, passes into *tetroxide* K_2O_4. This *tetroxide* when treated with water breaks up into oxygen and a solution of dioxide. The solution of either dioxide is stable at low temperatures; but when boiled it is decomposed with evolution of oxygen, and ultimately converted into one of hydrate RHO. The *dioxides* when added to an excess of *cold dilute acid* yield alkaline salts and *peroxide of hydrogen* H_2O_2.

Alkaline Salts.

253. 1.—Generalities; solubility-relations.—Of the vast number of salts producible by the direct action of *caustic alkalies* on properly so-called *acids*, the great majority are readily soluble in water, and none are quite insoluble; in fact there is no such salt known, which was 'insoluble' in water even to the extent, say, of sulphate of strontia. All alkaline salts not derived from coloured acids are colourless. From their solutions they can generally be obtained in *crystals*, which in many cases contain crystal-water. Speaking in reference to a considerable number of acids, we may say that, in general, potassium, rubidium, and cæsium salts are less prone to take up crystal-water, and are less soluble in water than the corresponding sodium compounds; and that, if an acid forms a less soluble salt with potassium than with sodium, the rubidium and cæsium salts are at least as little soluble as, and often less soluble than, the potassium compound. Of normal *alkaline salts*, those derived from *strong mono-* or *di-basic acids* (such as HCl, HBr, HI, HNO_3; H_2SO_4, $H_2C_2O_4$, etc.) are *neutral* to litmus and turmeric paper; the normal *arseniates* and phosphates $(P_{or}As)O_4.R_3$, are strongly alkaline; the normal salts of *acetic* and higher fatty acids, like those of all other weak acids, colour red litmus blue. The *cyanides* RNC and *carbonates* R_2CO_3 are almost as strongly alkaline to *litmus* and *turmeric* as the hydrates.

2. Behaviour to heat. An alkaline salt, when kept at a dull red heat in a close crucible, *may get decomposed*, but is sure *not* to lose any alkali-metal. (Compare chapter on ammonium salts.) Of those which, under these circumstances, suffer no *chemical* change, The *chlorides*, *bromides*, *iodides*, *cyanides*, melt at an incipient red heat into colourless fluids, which at higher temperatures are more or less slowly volatilized ;

The *carbonates* R_2CO_3 require a full red heat for being fused, when they, generally, suffer a slight loss of carbonic acid. At very high temperatures they are volatilized ;

The *sulphates* R_2SO_4 behave, substantially, like the carbonates, with this difference, however, that they lose *no acid ;*

The *phosphates* $P_2O_5.2R_2O$, *borates* and *silicates* are more stable and less volatile than even the sulphates.

Of salts *decomposible* at a *dull red heat*, the following may be named :—

The *nitrates*. These are decomposed, with formation of, first, *nitrite*, and then, especially on the application of a stronger heat, of oxide or peroxide.

The *acid carbonates* $RH.CO_3$ when heated are readily reduced to normal carbonates.

The *acid sulphates* $RH.SO_4$, at a bright red heat, are reduced to normal sulphates R_2SO_4.

Salts of organic acids (except the cyanides RNC and carbonates R_2CO_3) when exposed, for a sufficient time, to a red heat are decomposed so that the alkali ultimately remains as *carbonate*, mixed, in general, with more or less of carbon, and not unfrequently containing, in this case, an admixture of *cyanide*.

Almost all alkaline salts when directly exposed in small quantities to the flame of a Bunsen's lamp, or to a mouthblowpipe flame, undergo partial dissociation, with formation of *vapour of metal*. The phosphates P_2O_5 ($1R_2O$ or $2R_2O$), the more acid *silicates* and the *borates*, under these circumstances, exhibit an exceptionally high degree of stability.

254. *Table* showing the solubilities of some Potassium Salts as compared with the corresponding Sodium compounds.*

Denomination.	Potassium Salt.	Sodium Salt.
Chloride.	KCl, soluble at 15°·6 in 2·85 100° in 1·77 parts of water. Far less soluble in strong hydrochloric acid.	NaCl, soluble at 14° in 2·79 100° in 2·73 parts of water. Far less soluble in strong hydrochloric acid.
Nitrate.	KNO_3. soluble at 18° in 3·45 97° in 0·42 parts of water. Far less soluble in strong nitric acid.	$NaNO_3$, soluble at 18°·5 in 1·14 119° in 0·46 parts of water. Less soluble in nitric acid (?)
Sulphate (acid).	$KHSO_4$ Easily soluble.	$NaHSO_4(+xH_2O)$ Easily soluble.
Sulphate (normal). See note (1).	K_2SO_4 100 parts of water dissolve at t°. (8·36 + 0·1741 t.) parts.	$Na_2SO_4 . 10H_2O$ 100 parts of water dissolve— at 15°— 34 } parts of cryst. at 36°—412 } salt ($10H_2O$). On boiling at 103°, 42·6 parts of Na_2SO_4.
Carbonate (acid).	$KHCO_3$ 1 part of salt dissolves— at 20°—70° in 3·72—2·21 parts of water.	$NaHCO_3$ 1 part of salt dissolves— at 20°—70° in 8·97—5·98 parts of water.
Carbonate (normal). See note (2).	$K_2CO_3 \{+ 2H_2O\}$ 1 part of K_2CO_3 dissolves— at 12°—70° in 0·9—0·49 parts of water.	$Na_2CO_3 + 10H_2O$ 1 part of salt dissolves— at 14°— 36°—104° (boiling). in 1·66—0·12—0·22 pts. of water.
'Alum.' See note (3).	$Al_2O_33SO_3 . K_2OSO_3 + 24H_2O$ 1 part of salt dissolves— at 10°—100° in 10·5—0·28 parts of water.	$Al_2O_33SO_3 . Na_2OSO_3+24H_2O$ soluble in about its own weight of cold water.
Perchlorate. See note (4).	$KClO_4$ 1 part of salt dissolves— at 15°—100° in 65—much less of water. Insoluble in abs. alcohol.	$NaClO_4$ deliquescent, very easily soluble in water; soluble in alcohol.

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* The formulæ refer to the salts as they are when crystallized from water under ordinary circumstances.

Denomination.	Potassium Salt.	Sodium Salt.
Oxalate (normal).	$K_2C_2O_4H_2O$ soluble in 3 parts of cold water	$Na_2C_2O_4$ 1 part of salt dissolves— at 15°—boiling temp. in 31—16 parts of water.
Tartrate (normal).	$K_2C_4H_4O_6$ 1 part of salt dissolves— at 14°—64° in 0·66—0·47 parts of water.	$Na_2C_4H_4O_6 + 2H_2O$ 1 part of salt dissolves— in 5 parts of cold and in much less of hot water.
Tartrate (acid). See note (5)	$KH.C_4H_4O_6$ 1 part of salt dissolves— at 15°—100° in 222—14·5 parts of water.	$NaH.C_4H_4O_6 + H_2O$ 1 part of salt dissolves— in the cold — on boiling in 9 — 1·8 pts. of water.
Silicofluoride. See note (6)	K_2SiF_6 1 part of salt dissolves— at 17°·5—boiling temp. 833—105 parts of water.	Na_2SiF_6 1 part of salt dissolves— at 17°·5—101° (boiling temp.) in 153—40·7 parts of water.
Chloroplatinate. See note (7)	K_2PtCl_6 1 part of salt requires— at 15°—100° 100—19.3 parts of water. Of alcohol (ord. temp.) of 97— 76— 55 per cent. 12080—3775—1053 parts.	$Na_2PtCl_6 + 6H_2O$ easily soluble in water and alcohol.

NOTES.

1. 100 parts of water at 70° dissolve 42·4 parts of *sulphate of rubidium*.

2. *Carbonate of cæsium* dissolves in almost any proportion of water. 100 parts of *absolute alcohol* of 19° dissolve 11 parts of the salt. The potassium and sodium salts are practically insoluble in absolute alcohol.

3. 100 parts of water of 17° dissolve, of

Potassium-	Rubidium-	Cæsium-Alum.
13·5	2·27	0·62 prts.

4. One part of *perchlorate of rubidium* dissolves in 92 parts of water of 21°·3.

5. One part of *bitartrate of rubidium* dissolves in 84·5 parts, one part of the *cæsium* salt in 10·3 parts of water of 25°.

6. All alkaline *silicofluorides* are *insoluble* in alcohol. The *rubidium* salt dissolves in 614 parts of water at 20°; the *cæsium* salt in 166 parts of water of 17°.

7. 100 parts of water of t° dissolve, of

t	K_2PtCl_6	Rb_2PtCl_6	Cs_2PtCl_6
10	0·9	0·15	0·05
50°	2·2	0·20	0·18
100°	5·2	0·63	0·38 parts.

Behaviour of moderately concentrated aqueous solutions of alkaline salts to Reagents.

255. Hydrofluosilicic acid produces a precipitate of fluosilicate SiF_6R_2, which, however, being semi-transparent, is distinctly visible only after settling, when it appears as a bulky, apparently amorphous, deposit, although in reality it consists of microscopic crystals. If, besides an excess of reagent, a sufficiency of *alcohol* be added, and the mixture allowed to stand for some hours, the precipitation, especially in case of potassium [and rubidium] is almost complete. Hence the reagent, when used in conjunction with alcohol, may serve to separate the whole *group* of metals we have here to deal with, not only from the acid radicles they may be combined with, but also from magnesium, strontium, calcium, and other metals forming *fluosilicates soluble in alcohol.*

256. A solution, saturated in the cold, of *bitartrate of soda*, of course, does *not* precipitate *soda salts*, but when added to a solution of *potash* [or rubidia] salt, produces a crystalline precipitate of bitartrate, which, however, in dilute solutions, if at all, appears only after some time. Its formation is promoted by stirring. In the case of hydrates, carbonates, or cyanides, (an excess of) *tartaric acid* must be substituted for the soda salt. The acid, in fact, might be used in all cases, but the bitartrates being far more soluble in even dilute acids than in neutral salt solutions, the soda salt is preferable as a general reagent.

257. A concentrated solution of *chloride of platinum* when added to one of chloride of *potassium* [*rubidium* or *cæsium*] produces a yellow crystalline precipitate of chloroplatinate, in which, by and by, the *bulk* of the metal accumulates. In the case of other salts than the chloride, *hydrochloric acid* must be added in conjunction with the reagent in order to virtually convert the alkali metal into chloride; but the reaction then, on account of the presence of free acid, is less sensitive. In all cases the precipitation is more complete on addition of *alcohol.* *Sodium salts*, under all these circumstances, are not precipitated by the reagent. It is, however, to be remarked that *sulphate* of sodium, when its aqueous solution is mixed with alcohol, is precipitated *as such*, even in presence of excess of chloride of platinum.

A glance at the table in § 254 will show what degree of sensibility these precipitating tests can be expected to possess.

258. Meta-antimoniate of potassium, $K_2OSb_2O_5.7H_2O$, has been recommended as a specific precipitant for *sodium.* The precipitate is at first flocculent but becomes crystalline on standing. In dilute solutions the precipitate takes more or less time in forming; one part of sodium salt in 1000 parts of water becomes visible after twelve hours. The solution must be neutral, or slightly alkaline, and not contain any foreign metals except potassium. To prepare the reagent, mix equal parts of *tartar emetic and nitre*, and project the mixture, small quantities at a time, into a red-hot hessian crucible. After complete deflagration, maintain a dull red heat for about a quarter of an hour, then allow to cool, and treat the mass with warm water. Wash the granular precipitate formed and dry it on bibulous paper. The solution for testing should be made *ex tempore*, by shaking a few granules of the salt with cold water.

259. A hydrochloric solution of *terchloride of antimony*, when added to hydrochloric solutions of *cæsium* salts, produces a crystalline precipitate $SbCl_3CsCl$, which is decomposed by water, but can be washed without decomposition with concentrated hydrochloric acid. The chlorides of the other three alkali metals and chloride of ammonium are *not* precipitated.*

Flame Tests.

260. Almost all alkaline salts when exposed, in small quantities, to the *direct* action of a *Bunsen's flame*, undergo dissociation, with formation of vapour of metal, which, in each case, emits a particular kind of light characteristic of the metal; and, on the flames being viewed through the spectroscope, each of the metals is found to yield a peculiar spectrum. The *potassium*, *rubidium*, and *cæsium* flames are *violet*, and can scarcely be distinguished by the eye, but their spectra differ: the *potassium* spectrum consists mainly of two lines, a comparatively strong line in the *red*, and a faint line in the blue. The spectra of *rubidium* and *cæsium* are far more complex, consisting each of a large number of lines, of which, in the case of *rubidinm*, a *red* line, and a *double violet* line, more refrangible than the G line of the solar spectrum, and in the case of *cæsium* two *blue* lines, lying between the solar lines F and G, are most characteristic.

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* *R. Godefroy*, Ber. d. Deutschen Chem. Gesellschaft for 1874, page 375.

The *sodium* flame is *intensely yellow*; its spectrum consists of a double line coinciding exactly with the D line of the solar spectrum. The tests founded upon these facts are extremely delicate, which must be borne in mind in their application. This holds more especially with sodium, of which as little as $\frac{1}{3000000}$th of a milligramme is sufficient to colour a gas flame distinctly yellow, while far less suffices to produce a visible spectrum. A *mixture* of sodium and potassium [Ru,Cs] salt, unless the potassium predominates *very largely*, produces a *yellow* flame, which by the eye cannot be distinguished from a pure sodium flame; but the spectroscope, if the *sodium* does not predominate *too much*, will always enable one to see at least the *red* potassium line distinctly. Of alkaline salts, not dissociable in a Bunsen's flame, the more acid borates, silicates, and phosphates, and a large class of native alkaliferous silicates, are the most important. Such substances must, previous to the application of the flame test, be moistened with hydrochloric acid, or if not affected by this agent, be mixed with excess of pure *sulphate of lime*. By the action of this reagent a part at least of the alkali metal is (as a rule) converted into sulphate which gives a decided flame colour and spectrum.

Appendix on Ammonium.

261. '**Ammonium**' is the name given to the residue NH_4, which, in 'ammonium' salts, plays the same part as 'K' in potassium, and 'Na' in sodium salts. The radicle has never been isolated.

262. Ammonia NH_3 is a colourless gas of the spec. grav. 0.597 (Air=1), condensible into a liquid which, under ordinary pressure, boils at −40° C. The gas possesses a very strong characteristic odour. It is very largely soluble in water, the more so the lower the temperature. One gramme of water, at 16° C., and under a partial pressure of 760 mm., absorbs 0·582 grms. of the gas. The aqueous solution is lighter than water. When boiled, it readily gives off its dissolved gas; when exposed to the air it gradually loses its ammonia by absorptiometric exchange for air; hence even very dilute solutions smell strongly of the gas.

263. Ammonia, even if anhydrous, colours red litmus blue, and yellow turmeric brown. It unites directly with all properly so-called acids forming ammonium salts. Ex.: $SO_4H_2 + NH_3 = NH_4.H.SO_4$.—$NH_4HSO_4 + NH_3 = (NH_4)_2SO_4$. The same reactions go on in aqueous solutions; in fact a solution of ammonia in water behaves to acids exactly like one of caustic soda or potash; it may therefore be looked upon as one of an unstable hydrate $NH_4.HO$, analogous to KHO.

264. Ammonium salts, generally, are similar in their properties to the corresponding salts of *potassium;* not so much to those of sodium. Most of them are easily soluble in water; the 'alum,' bitartrate and chloroplatinate, however, are (like the corresponding potassium salts) difficultly soluble, while the perchlorate (unlike $KClO_4$) is easily soluble in (5 parts of) water. To what has already been said, it is scarcely necessary to add, that the behaviour of *solutions of* *ammonium salts* to *tartaric acid* and to *chloride* of *platinum* is the same as that of potassium salts: it is however to be observed that while *tartaric acid* is not by any means so sensitive a precipitant for ammonium as for potassium, the two *chloroplatinates* [$PtCl_6K_2$ and $PtCl_6(NH_4)_2$] are almost identical in appearance and solubility relations. Ammonium salts are easily distinguished from the salts of the alkali metals,

265. 1. *By their comportment on exposure to a dull red heat.* At this temperature all those ammonia salts which are derived from volatile acids are completely volatilized; [the cyanide $NC.NH_4$ without decomposition; the haloids (NH_4Cl, NH_4Br, NH_4I) with formation of dissociated vapours; the sulphates with formation of a mixed vapour of nitrogen, water, ammonia, and sulphurous acid; the nitrate with formation of water and nitrous oxide], while those derived from non-volatile acids *ultimately* leave residua of acid (ex.: the phosphates), or acid anhydride (ex.: molybdate, tungstate*), or of some reduction product of the acid anhydride (ex.: the chromates, which leave Cr_2O_3; the chloroplatinate, which leaves *metallic platinum*).

2. By *their* giving off *ammonia* when heated with solution of *caustic soda* or *milk of lime.* The liberated ammonia, even if largely diluted with air, can be recognised (1) by its pungent smell; (2) by its action on red litmus or turmeric; (3) by its forming dense clouds (of solid NH_4Cl) when brought in contact with a glass rod moistened with *dilute* hydrochloric acid; (4) by its actions on *mercurous nitrate* or *manganous* sulphate (which result in the formation of a *black* amido-compound and of *brown* sesquihydrate of manganese, respectively); and, if all these tests fail, (5) by means of

266. 'Nessler's reagent' (*i.e.* a solution of mercuric iodide in a mixed solution of iodide of potassium and caustic potash or soda).* If an *excess* of this reagent is added to an aqueous solution of ammonia or of an ammonia salt, a brown precipitate is formed consisting of iodide of mercurammonium. [$4(HgI_2.2KI) + 6KHO + 2NH_3 = 14KI + 4H_2O + N_2Hg_4I_22H_2O$.] The precipitate is *soluble* in *ammonia salts;* by the action of caustic soda and sulphide of sodium in the heat it is decomposed, with elimination of the whole of the nitrogen as ammonia. In *very* dilute solutions the reagent produces only a brown colouration, which, however, is so intense, that $\frac{1}{200}$th part of a milligramme of ammonia in 100 c.c. of water is clearly indicated. —(*Wanklyn and Chapman.*)

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* In these cases some metallic nitride is found in the residuum.

268. To test a solution of salts for *combined ammonia*, mix it in a beaker with excess of caustic soda (or milk of lime), and heat gently. If no ammonia can be detected with certainty by the smell, or by means of a glass rod moistened with dilute hydrochloric acid, cover the beaker with a glass plate to which a bit of filter-paper moistened with one of the ammonia indicators, mentioned (under 2, 4, or 5 in § 265), has been previously attached, and keep the whole for a time at a gentle heat. The ammonia, if present, will gradually accumulate in the reagent, and at last produce a visible effect. A more refined method is to distil the mixture out of a retort connected with a *Liebig's* condenser, and next to search for ammonia in a few drops of the distillate with *Nessler's reagent.* In case of a positive result, the rest may be used for confirmatory tests with less sensitive reagents, to enable one to form at least an idea of the quantity of ammonia present.

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* **267.** To prepare this reagent: Dissolve one part of *iodide of potassium* in one part of water, and add to the solution, with continuous agitation, of a solution, saturated in the cold, of *mercuric chloride*, until the locally formed precipitate of HgI_2 no longer disappears on agitation. Filter, add a concentrated solution of four parts of *caustic potash*, and dilute to the volume of 20 parts of water (*e.g.* to 1 liter if 50 grammes of iodide of potassium were used). At last add $\frac{1}{10}$ vol. of a saturated solution of mercuric chloride, allow the mixture to settle in a stoppered bottle, and decant, or filter.—(*Wanklyn and Chapman.*)

269. In the analysis of a solution which has *not* been *proved* to be free from *nitrates* and *nitrites*, the examination for ammonia must take place previous to the application of *sulphuretted hydrogen* even, because, at least, traces of NH_3 may be formed by the action of this reagent on acid solutions of the two classes of salts named.*

270. *Methylamine*, $NH_2.CH_3$, *Dimethylamine*, $NH(CH_3)_2$, *Ethylamine*, $NH_2.C_2H_5$, and some other organic *monamines*, closely resemble ammonia in their reactions, and are consequently liable to be mistaken for it. They can be distinguished from ammonia

(1.) By their containing carbon, and consequently, on combustion with *oxide of copper*, yielding carbonic acid; (2.) By the greater solubility of their *hydrochlorates* in *strong alcohol*, ordinary sal-ammoniac being almost insoluble in this menstruum; (3.) By the greater solubility in water of, and the *lower* percentage of platinum in, their *chloroplatinates*.

Examination of a solution of salts for the metals of the potassium group (and for lithium).

271. Given a solution of metallic salts, which, for the sake of greater generality we will assume to contain metals of the copper, arsenic, iron, and barium groups, but which, for the sake of simplicity,† we will suppose to be free from non-volatile non-metallic acids, except perhaps *phosphoric*, ——and the first step towards the solution of the problem formulated in the heading is, by the successive application of sulphuretted hydrogen, sulphide of ammonium, and carbonate of ammonia; or, if we prefer it, of sulphuretted hydrogen, sulphuric acid and alcohol, and sulphide of ammonium, to eliminate all that can be precipitated by these reagents, so that, ultimately, we obtain a filtrate which can contain no other metals than *Magnesium*, *potassium* [*rubidium*, *cæsium*, *lithium*], *and sodium.* We next test a portion of the filtrate for *magnesium* (according to § 238), by means of *alkaline phosphate.*

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* Private communication from Mr. J. Y. Buchanan.

† As well as not to anticipate what properly belongs to Division III.

272. *If magnesium is proved to be absent,* then *phosphoric acid* may be present, and if so, it had better be removed by some method or other which does *not* re-introduce any metals proper (*i.e.* anything except ammonia salts of volatile acids). Supposing this to have been accomplished, we need only evaporate the liquid to dryness, and, after having transferred the *dry* residue to a platinum crucible, ignite as long as any ammonia-salt vapours go off, to obtain a residue which must contain all that was present in the solution of *alkali metals* [and of lithium]. But it does not follow that the residue necessarily consists altogether of salts of the metals named, because, evidently, any trace of alumina, lime, or other constituent of the solution which, in the methods of separation previously employed, escaped precipitation, will necessarily find its way into the 'alkaline salts.' Hence the residue must not be accepted as being what, by theory, it ought to be, unless it (1.) is perfectly *white*, and (2.) is completely soluble in a small quantity of water, yielding a solution which, on addition of a drop of *sulphide of ammonium* and a *drop of carbonate of ammonium*, remains *clear.* If, on the application of these tests, insoluble matter is left or separates out, the mixture must be filtered, the filtrate evaporated, and the residue ignited, when a product will be obtained which, in general, may be looked upon as really consisting (potentially) of salt of potassium [rubidium, cæsium, lithium], sodium, and nothing else. The least quantity of such residue will suffice for a complete (virtual) analysis by means of the spectrum-apparatus, but unfortunately spectrum tests, just on account of their wonderful sensibility, are liable to tell more than the truth : which in this case means more than the practical analyst cares to know. It is to be observed, also, that the traces of alkali which, in the course of the previous separation, were extracted from the glass vessels used, or introduced as impurities in the reagents, will necessarily get mixed up with the alkaline salts from out of the substance

under examination. Hence, even in qualitative analyses, a rough guess, at least, must be made of the *quantities* of potassium or sodium, etc., found, or the results are of no practical value. Methods for this purpose will be readily deduced from what now follows.

Separation of Potassium from Sodium.

273. (*a*) *The metals are given as chlorides.*

This is the easiest case. We need only dissolve the chlorides in water, add excess of *chloride of platinum*, *i.e.* enough to convert *both* metals into chloroplatinates, evaporate to a very small bulk, so that the residue, after cooling, forms a paste, and then add a quantity of 80°/$_0$ *alcohol*, in order to obtain the *potassium* for itself, in the form of a precipitate of chloroplatinate (which must be washed with alcohol until the liquid runs through colourless). The *sodium* passes into the filtrate as chloride, which, after removal of the alcohol by evaporation, and precipitation of the *platinum* by *hydrogen* (see § 106), can be obtained by evaporation to dryness.

274. (*b*) *The metals are given as neutral sulphates.*

In this case *one* method is, to repeatedly ignite the sulphates with much sal-ammoniac, and thus to convert them into chlorides, which may then be separated as shown under (*a*); but far better results are obtained by applying *Finkener's* method, which is as follows:—Dissolve the sulphates in the least quantity of water, and add in the cold enough of a concentrated solution of chloride of platinum to convert the *potassium* into chloroplatinate, *i.e.* so much of the reagent that the liquid, after the precipitate has settled, appears yellow; next evaporate on a water bath until the residue, after cooling, forms a paste; mix this paste, gradually, with 15-20 volumes of a mixture of two volumes of *absolute alcohol* and one volume of *ether;* allow to settle, and wash the precipitate with the same liquid until the last drops run off colourless. The precipitate contains *all the* *potassium*, as K_2PtCl_6 and the *bulk* of the *sodium* as Na_2SO_4, which latter salt can be extracted by treatment with a cold concentrated solution of *sal-ammoniac.*

275. (*c*) *The metals are given, partly at least, as phosphates, borates, or salts of other acids not sulphuric or hydrochloric.*

In this case a perfectly exact separation is difficult, but an approximately complete precipitation of the potassium at least can be effected by dissolving the mixture in a small quantity of dilute hydrochloric acid, adding excess of concentrated chloride of platinum, and lastly a large quantity of *ether-alcohol* (vide *supra*). The potassium is precipitated as chloroplatinate, which, after having been washed, first with ether-alcohol acidulated with hydrochloric acid and then with pure ether-alcohol, is practically pure.

276. If any of these three methods is applied to a substance containing *lithium*, *rubidium*, or *cæsium*, then the *lithium* passes into the *filtrate* along with the sodium (or, in the case of (*b*), part of the sodium) from which—after removal of the alcohol by evaporation, and of the platinum by means of hydrogen—it can be separated out either by precipitation in the form of *phosphate* (§ 245), or—after conversion of the two metals into *dry* chlorides—by means of *ether-alcohol* (§ 243). The *rubidium* and *cæsium* pass into the potassium precipitate, in which, if they form a considerable fraction of the whole, they may be detected by means of the spectroscope. Straightforward methods for the separation of the three metals from one another have not yet been discovered, but if a sufficient quantity of the mixed chloroplatinates can be procured, a portion of the two rare metals can be eliminated by boiling the precipitate repeatedly with small quantities of water, until the potassium salt is extracted, *i.e.* until the residuum no longer yields a potassium spectrum, and consequently consists of the chloroplatinates of rubidium and cæsium only. (Comp. § 254.) In these operations a large portion of these two metals, of course, passes into the filtrates, from which they can be precipitated by means of alcohol as parts of a mixed chloroplatinate, from which, by a repetition of the process of fractional solution, an additional quantity of rubidium and cæsium salt can be obtained, etc. etc. To obtain the alkali metals in a soluble form, and to recover the platinum, the chloroplatinates are reduced by means of hydrogen at a temperature just *below* the fusing point of the mixed chloride, which subsequently is extracted and separated from the metallic platinum, by means of water. From a concentrated hydrochloric solution of a mixture of the chlorides of rubidium and cæsium, the latter metal can probably be precipitated, free from the other, by means of terchloride of antimony. (See § 259.)

If magnesium is present

277. (in the filtrate referred to in § 271), then this metal must first be eliminated before a satisfactory separation of the alkali metals can be effected. For this purpose a great many methods have been proposed, of which the following are perhaps the best that can be adopted for qualitative purposes:—

(*a*) *The phosphate method.*

278. (After due concentration of the liquid) add a large excess of concentrated ammonia, *i.e.* so much that the mixture ultimately contains about 5°/₀ of *free* NH_3, then add enough of pure *phosphate of ammonia* to convert the magnesium into PO_4MgNH_4, allow to stand for some hours, filter and wash the precipitate with *dilute ammonia.* From the filtrate next boil off the excess of ammonia, dilute with water, add excess of *ferric chloride* (*i.e.* considerably more than 'Fe_2O_3' for every 'P_2O_5'), then again a *slight* excess of ammonia, and at last boil off that excess and filter. The precipitate contains all the iron and all the phosphoric acid; the filtrate contains the alkali metals and ammonia salts, and after expulsion of the latter by evaporation and ignition, may be analysed as shown in § 272 *et seq.*

(*b*) *The baryta or lime method.**

279. Evaporate to dryness, burn off the ammonia salts, and if the metals are present as sulphates, convert these, at least partially, into chlorides by repeated ignition with salammoniac. Now treat with water, and, without removing the oxychloride of magnesium that may separate out, boil with excess of *baryta-water* or *milk of lime*, and filter. The precipitate contains the magnesium as oxide; the filtrate contains the lithium and alkali-metals beside barium or calcium, of which two metals either can easily be removed by precipitation with *carbonate of ammonia* in the heat, so that at last a filtrate is obtained which can be analysed according to § 272 *et seq.*

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* This method is applicable also in presence of iron, alumina, and manganese; part of the alumina, if baryta be used, passes into the filtrate but is subsequently eliminated by the carbonate of ammonia.

(*c*) *The carbonate of ammonia method.*

280. (After complete elimination of the ammonia salts) dissolve in the *least quantity of water*, add a large excess of a concentrated solution of *neutral carbonate of ammonia* $(NH_4)_2CO_3$ (comp. § 237), and allow to stand for twelve hours. The precipitate contains, practically, the whole of the magnesium as $Mg(NH_4)_2C_2O_6.4H_2O$, which must be washed *with the reagent.* The filtrate—apart from a trace of magnesium—contains no metals but K, Na [Li, Rb, Cs] and (NH_4). *This* method, in qualitative analyses, would deserve the preference before any other, if it was not the case that part at least of the potassium is always precipitated along with the magnesium, from which, however, it may be separated by igniting the precipitate, and from the residue $(MgO+xK_2CO_3)$ extracting the potash salt with hot water.

Note.—If methods (*a*) and (*c*) are applied in presence of *lithium*, a part of this metal may pass into the magnesium precipitate.

281. *General scheme for the exhaustive analysis of a complex of metals, given in the form of an aqueous solution of salts.*

Under this heading we propose to supply to the student an index to the several methods given in previous chapters, for the examination of salt-solutions for certain *groups* of metals, and shortly to sum these up into a general scheme of analysis. But none of these methods being free from assumptions regarding the *nature* of the salts present, the general scheme to be deduced from them must *a fortiori* be of limited applicability; we shall therefore begin by giving a

282. *List of the classes of salts which in the instruction to be given* (in §§ 283-292) *are, in general, assumed to be* **absent.**[*]

(1.) Thiosalts, *e.g.* thiarseniates, thiantimoniates, etc. (Ex.: $As_2S_53K_2S$).
(2.) Thiosulphates, polythionates.
(3.) Complex cyanides generally, and more especially 'metallocyanides,' such as ferrocyanides, cobalticyanides, etc.
(4.) Pyrophosphates, metaphosphates.
(5.) Salts of organic acids, except carbonic, oxalic, succinic, and some others.
(6.) Silicates [tungstates, molybdates, vanadates].
(7.) Fluorides.

Supposing then, in the course of the examination of a substance, we had obtained an aqueous solution, which, from what we knew of the general nature of that substance, and from the way in which we had disintegrated it, could contain nothing but (say) metallic or hydrogen salts of nitric, hydrochloric, hydrobromic, hydriodic, phosphoric acid, or of oxygen acids of the halogens, or of sulphuric, sulphurous, or dithionic acid, or of any metallic acid not included in (6). Then the following scheme may be laid down for the exhaustive examination of the solution for metals:—

283. We first observe, and draw what conclusions we can from, the smell and colour of the solution and its action on test-papers; and next proceed to a cursory application, to separate small portions of the liquid, of a proper selection of metal-precipitants, *e.g.* hydrochloric acid, sulphuric acid, sulphuretted hydrogen, sulphide of ammonium, etc. At this stage of the investigation it is chiefly the *negative* results which are worth noting down and interpreting. A solution, for instance, which gives no precipitate on addition of *hydrochloric acid* need not be examined for silver and mercurosum, and cannot contain much lead; a solution which remains clear when heated with excess of *dilute sulphuric acid*, is free from barium, strontium, and lead, and can contain only traces of mercurosum. A *colourless* solution is by this property almost proved to be free from permanganates, manganates, chromates, chromic salts, and is not likely to contain large quantities of cobalt, nickel, copper, gold, platinum, and other coloured salts. In the interpretation of colours, however, we cannot be too cautious, because there is no saying what may not be the result from the simultaneous presence of a number of coloured constituents. Two solutions possessing complementary colours, as cobalt and nickel solutions, will, when mixed together in the right proportion, give a colourless fluid. If none of these tests and observations give positive indications, we evaporate some of the solution to dryness at a gentle heat to see if it contains any solids, and, if there is a residue, we see whether or not it volatilizes on exposure to a dull red heat. If it does so completely, the solution is not likely to contain any metals others than ammonium, mercury, arsenic, or perhaps antimony, tin, bismuth (these latter forming volatile chlorides). Let us now suppose, for the sake of greater generality, that these preliminary tests had *not* given direct evidence of the absence of any class of salts, and show how the complex of metals potentially present can be split up into groups.

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[*] Although in many cases a slight modification of the method in this part or that might bring them within its range of applicability.

284. If the liquid under examination is neutral or alkaline, we begin by acidifying it by gradual addition of *hydrochloric acid*. If the acid at first produces a precipitate which dissolves in additional reagent, this points to the presence of some insoluble metallic acid, such as Al_2O_3, ZnO, Cr_2O_3, SnO_2, Sb_2O_5* A permanent precipitate can contain nothing but *silver*, *mercurosum*, *lead* [and thallium]—as chlorides.* (Comp. note 1.) Regarding thallium, see § 176 *et seq.*; if it is absent, the other three can be separated from one another, as shown in § 33. The filtrate, if a sufficiency of hydrochloric acid was added, but an immoderate excess avoided, will be free from silver and mercurosum, but it may contain mercuricum and any of the rest of the metals. All this holds for a liquid which, from the first, possessed an acid reaction.

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* MoO_3 and V_2O_5 we should have to add, if we had not supposed these to be absent.

285. The filtrate now (assuming it to *contain* nitric, chloric, or other non-metallic oxidizing acids) needs only be freed from these by evaporation with excess of hydrochloric acid to a small bulk (see note 2), and the residue be diluted with water to be ready for the precipitation of the *arsenic* and *copper groups* by means of *sulphuretted hydrogen* (§§ 36, 39). If, however, there is any reason to suspect the presence of *gold* or *platinum*, it is as well to test small portions of the liquid for these two metals (§§ 73, 77, 106), and, in the remainder (if necessary), after removal of the free acid, to precipitate the two noble metals by means of *hydrogen*† (§ 106), and remove them by filtration. From the filtrate, after addition of the requisite quantity of hydrochloric acid and water, the copper and arsenic group metals are easily eliminated, by saturating the liquid with sulphuretted hydrogen, first at about 60–70° C. (to make sure of the *arsenic acid*), and then in the cold (to eliminate the last remnants of cadmium,‡ lead, bismuth, antimony,‡ and tin. The *precipitate*, after having been washed, first, in the cold with water containing some H_2S (in order to keep the sulphides CuS [SnS, SnS_2?] from getting oxidized by the action of the atmosphere), and then, after removal of the bulk of the free acid, with hot water, is treated repeatedly, at a gentle heat, with *yellow sulphide of ammonium*, when *arsenic, antimony, and tin* pass into the filtrate (from which they are re-precipitated by acidification with hydrochloric acid) while the *copper-group sulphides* remain undissolved. The arsenic group precipitate can be examined according to §§ 104 *et seq.;* regarding the copper group see §§ 36, 39. (Comp. note 3.)

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* WoO_3 would have to be named here, if it was not supposed to be absent.

† If platinum was found absent, some of this metal must be added (in the form of $PtCl_4$) to cause the gold to be precipitated; or else formic acid be used as a reducing agent.

‡ These two metals are particularly liable to escape precipitation in the presence of an excessive quantity of free mineral acid. On the other hand, *zinc*, and, next after it, nickel, cobalt [and thallium] may be named as being those metals of the iron group which require comparatively large quantities of ree mineral acid to keep them out of the sulphuretted hydrogen precipitate.

286. The *filtrate* from the sulphuretted hydrogen precipitate may contain any metals of the *iron, magnesium, barium,* and *potassium groups.* Before attempting an analysis of this possibly very numerous complex of metals, it is advisable first, by a series of preliminary tests, to try and form an idea of its composition. We consequently, first of all, observe the *colour* of the filtrate F, and compare it with that of the original liquid L.

287. If

L was	and F is	This indicates* the presence in L and F of salts of	
		L	F
Yellow or brown,	Colourless,	Fe_2O_3	FeO
Yellow or garnet-red,	Green or violet,	CrO_3	Cr_2O_3
[Yellow,	Green,	UO_3	UO_2]
Dark green,†	Colourless,	MnO_3	MnO
Purple,	Colourless,	Mn_2O_7 or Mn_2O_3	$\}$ MnO
Pink,	Pink,	CoO	CoO
Green,	Green,	NiO, Cr_2O_3 or CuO	NiO, Cr_2O_3 or CuO
(Let us take this opportunity for stating that :)			
Colourless,	Blue or green,	WoO_3 or MoO_3	Lower oxides of Wo or Mo.

288. Whatever may be the result of these observations, we must try, by the examination of separate small portions of the filtrate (according to § 201), to see which of the available methods of group-separation is most likely to work satisfactorily. Of these methods the following are the most important.

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* (But does not prove.)

† Before acidification; an acid liquid cannot contain manganates.

289. Method I. After neutralization with ammonia and addition of sal-ammoniac, precipitate with *sulphide of ammonium*, and filter.

The Precipitate	**The Filtrate**
may contain Fe, Ni, Co, Mn, Zn [Ur] as sulphides; Al and Cr as oxides or phosphates. Ba, Sr, Ca, Mg, as phosphates, ammonio-phosphates, oxalates; Mg as aluminate. Traces of these four metals in other forms. Of all these compounds, NiS and CoS alone do *not* readily dissolve in cold dilute HCl. For further information see sec. 202-208.	may contain Ba, Sr, Ca, Mg, [Li], K, Na [Rb, Cs]. Add *carbonate of ammonia* and heat, and the Ba, Sr, Ca are precipitated as *carbonates* (§ 231); while Mg and the rest of the metals named remain dissolved. (§§ 238 and 272-280).

290. Method II. After peroxidation of the *iron*, add first *sal-ammoniac*, then, gradually, excess of ammonia, and lastly boil off the free ammonia and filter.

Then (substantially, and generally speaking)

The Precipitate	**The Filtrate**
may contain Iron, Chromium, [Uranium], } as oxides. Aluminium, as oxide* or phosphate. Barium, Strontium, Calcium, } as phosphates or oxalates. Magnesium, as ammonio-phosphate. Nickel, Cobalt, } as oxides. For further information see sec. 202 *et seq.*	may contain Ni, Co, Mn, Zn, Mg† (as ammonia double salts); Ba, Sr, Ca; and K, Na, [Rb, Cs]. For further information see sec. 204 and 205.

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* Also the rare earths (§ 127) and titanium (§ 128 *et seq.*)

† Also Beryllium.

291. Method III. Proceed according to § 225, *i.e.* after peroxidation of the iron and due concentration, *first* precipitate the *barium group* by means of *sulphuric acid* and *alcohol*, and then search for the rest of the metals in the filtrate.

292. After elimination of the copper, arsenic, iron, and barium groups, the liquid can contain only *magnesium*, [*lithium*], and *alkali metals*, which may be separated from one another by applying the methods given in §§ 271-280.

Ammonium must be searched for in the original liquid. (See §§ 268 and 269.)

293. NOTES.

1. From solution of salts *not* proved to be free from the substances enumerated in § 282, excess of *hydrochloric acid*, in its capacity as an *acid*, may precipitate a great variety of things, besides AgCl, HgCl, $PbCl_2$, TlCl, *e.g.*,

(*a*) Tungstic and silicic acid, mixed possibly with stannic and titanic acids.

(*b*) Yellow sulphur : from thiosulphates or polythionates.

(*c*) White milky sulphur ; sulphides of the arsenic group ; sulphide of nickel. The formation of these metallic sulphides would generally be accompanied by an evolution of sulphuretted hydrogen; not necessarily though, because alkaline cyanide, for instance, might have served as a solvent.

(*d*) Insoluble cyanides. In this case, as a rule, hydrocyanic acid would be liberated, which could be separated out by distillation.

(*e*) Iodine : in consequence of the presence of iodides along with certain oxidizing, or iodates along with certain reducing, agents,

(*f*) from comparatively concentrated solutions : boracic acid ; also benzoic and other difficultly soluble organic acids.

It is hardly necessary to point out that these substances could not possibly be all present together in the same precipitate.

2. This operation ought, by rights, to be carried out in a retort connected with a receiver, because, as soon as the concentration of the residue has gone beyond certain limits, *arsenic*, antimony, tin, and bismuth are liable to be volatilized as chlorides. (Arsenic, present as As_2O_5, is sure to remain in the residue.)

3. If *yellow* sulphide of ammonium is used, traces of copper and mercury may pass into solution, and will then get mixed up with the arsenic

group precipitate. Hence if, by one way or another, the absence of gold, platinum, and stannous sulphide has been demonstrated, the colourless reagent is preferable to the yellow one.

Let us take this opportunity for stating that, in certain cases, it is very difficult, if not impossible, to extract, by sulphide of ammonium, the last trace of arsenic group metals from a sulphuretted hydrogen precipitate. Thus, for instance, *arsenic* cannot, by means of the general reagent, be completely separated from copper. In *this special case*, a better method is first to dissolve the sulphides in hot sulphuric, with addition of nitric acid, and then to precipitate the sulphate of copper by addition of alcohol, or what is better, by means of *sulphate of ammonia* and alcohol. A similar method applies to *lead* and arsenic.

If a sulphuretted hydrogen precipitate, supposed to be free from, but really containing, arsenic group sulphides, were treated with boiling hydrochloric acid (in accordance with § 39), then the gold and platinum and the bulk of the arsenic would, in general, remain with the CuS and HgS, while the tin and antimony (and more or less of the arsenic) would go into solution along with the Cd, Pb, and Bi.

III.—NON-METALLIC ELEMENTS.

294. In this division we propose to develop methods—(1.) for the examination of a substance for its non-metallic elements; (2.) for the discrimination of all the more important inorganic, and of a few of the more common organic, acids; and (3.) for the separation from one another, and from metallic bases, of certain groups of these acids. Apart from the halogens which are treated as a genus, each element has a special chapter devoted to it, which always begins with an exposition of the properties and reactions of what is called the 'free element,' and then passes on to the consideration of those acids in which the element forms the characteristic ultimate radicle. At the end of each chapter it is shown how a complex of metallic salts of *these acids* can be exhaustively analysed; and at last methods are given, by means of which any of the *other* compounds of the element under consideration can be identified as *compounds of that element.* To avoid unnecessary repetition, let us state here, once for all, that in giving '*the reactions of the salts of an acid*' we have in view chiefly the *potassium*, *sodium*, and *ammonium* salts. The extent to which the respective tests and methods of separation apply to salts of other bases can generally be deduced from a consideration of the properties of those products which, supposing the reaction did hold, would be formed; from their solubility relations, degrees of volatility, colours, for instance, if the test we have to deal with is founded upon the formation of an insoluble, a volatile, or a characteristically coloured substance, respectively.

THE HALOGENS.

(CHLORINE, BROMINE, IODINE.)

295. In order to be able to shortly state what is common to the three elements, or to two of them, we shall use the following generic words and symbols, viz.:—

'*Halogen*' for Chlorine, Bromine, Iodine.
'X' ,, Cl Br I
'*Haloid*' ,, Chloride, Bromide, Iodide.
'RX' ,, RCl RBr RI
'*Halogenate*' for Salts of oxygen-acids of the halogens.

I. *The Free Halogens.*

296. Physical properties.—*Chlorine*, Cl_2, a yellowish-green *gas* of the spec. gr. 2·44 (air = 1), which, when subjected, at ordinary temperatures, to a pressure of about five atmospheres, condenses into a yellow liquid. *Bromine*, a dark-brown, almost non-transparent *liquid*, of the spec. gr. 2·97, which, even at the ordinary temperature, emits copious brown vapours. It freezes at −24°·5, and boils at 63°. *Iodine*, a black, non-transparent, metallic-looking, crystalline solid, of the spec. gr. 4·95, which, although possessing a very decided smell, does not, at ordinary temperatures, emit visible vapours. It melts at 113°-115°, and boils above 200°; but far below even the former temperature emits *violet* vapours, which are so intensely coloured that they are visible even when very largely diluted with colourless gases. Halogen-vapour generally exhibits a most violent action on the respiratory organs, which only after large dilution with air assumes the character of a smell.

297. Solubility relations.—*Chlorine* is absorbed by water, the more largely the lower the temperature. One gramme of water of 15°, when shaken with excess of pure chlorine of 760 mm. partial pressure, absorbs 7·52 mgr. of the gas = 2·37 cc. at 0°, and 760 mm. The solution ('chlorine-water') is yellowish green; the dissolved gas is readily expelled by a current of any other gas or by boiling.

Bromine and *iodine* also are only sparingly soluble in water. When saturated at 15° and 6° respectively, *bromine-water* contains 3·23 p. c. (*W. Dancer*), and *iodine-water*, $\frac{1}{66000}$th of its weight of halogen. Both halogens are more largely soluble in solutions of the corresponding *hydrogen*, *potassium*, and *sodium salts* than in pure water. All these aqueous solutions, if sufficiently rich in free halogen, exhibit a *brown* colour; but, whatever may be their degree of concentration, the free halogen is easily expelled by *boiling*, and can be extracted by shaking the solutions with *bisulphide of carbon* or *chloroform*, when, even if a comparatively small volume of one or the other of these liquids was used, the bulk of the free halogen passes into the *bisulphide* or *chloroform*, imparting to it, in the case of *bromine*, an intense *brown* (or yellow), in the case of *iodine*, a still *more intense violet*, colour.

Reaction on—

298. Oxygen (*i.e.* O_2), **Nitrogen, Carbon.**—These elements do not at any temperature act on free halogen or halogen-haloid.

299. Hydrogen.—A mixture of equal volumes of chlorine and hydrogen, when exposed to direct sun-light, is instantaneously and completely converted into hydrochloric acid HCl, with explosion. In diffuse daylight, or if a sufficient excess of one of the two gases is present, the same reaction progresses gradually and quietly. A mixture of *halogen-vapour generally*, and *hydrogen*, when passed through a *red-hot tube*, undergoes partial association into hydride XH; but while in the case of chlorine the whole of the potentially present HCl is actually produced, in the case of bromine a part of the H+Br, and in the case of iodine the bulk of the H+I, *escapes* association. Of the three hydrides, HCl, and in a limited sense also HBr, is stable at a red heat, while HI, at such temperatures, undergoes very large dissociation into I_2 and H_2.

300. Sulphur, Phosphorus, Silicon, Boron, are all capable of uniting directly at least with chlorine or bromine. Of the compounds producible in this way, the following are the most important:—S_2Cl_2, S_2Cl_4, PCl_3, PBr_3, PCl_5, PBr_5, $SiCl_4$, BCl_3. All these halogenides when treated with excess of water are decomposed with formation of oxygen acids of the element associated with the halogen and complete elimination of the latter as *hydride HX*. In the case of *phosphorus* the same products are formed by the simultaneous action of this element on water and halogen. Ex.: $P+Cl_5+5H_2O=PO.(OH)_3+H_2O+5HCl$.

301. Metals.—Halogen is capable of combining with all metals; with those of the potassium, magnesium, and barium groups, and with silver, zinc and cadmium only in the *one* proportion of one equivalent of metal to one equivalent of halogen ($R' : X$ or $R'' : X_2$); with most other metals in several proportions. The vast majority of these compounds can be produced by the direct union of the free elements, or—as aqueous solutions—by the simultaneous action upon one another of halogen, metal and water. *Iridium* is the only metal which is not attacked at the ordinary temperature by any halogen; *gold* and *platinum* are not affected by *iodine*. In affinity to hydrogen and electro-positive metals, and stability of the respective compounds, chlorine exceeds bromine, and bromine exceeds iodine. Hence chlorine decomposes bromides and iodides, and bromine decomposes iodides, with liberation of the respective halogens.

302. The following table shows the effect of a *current of dry chlorine* on some of those metals which are most likely to present themselves to the analyst in the free state. The action in each case is supposed to be started in the cold, and then to be supported, if necessary, by application of the requisite amount of external heat.

Symbols of the Metals.	Products of Chlorination.	Properties of Chlorides.
As, Sb, Sn, Bi.*	$AsCl_3$, $SbCl_5$, $SnCl_4$, $BiCl_3$.	Liquids, or readily fusible solids, distillable, without decomposition, at temperatures far below redness.
Fe, Al.	Fe_2Cl_6, Al_2Cl_6.	Solids sublimable in a dry current of chlorine below 200°.
Hg.	$HgCl$ and $HgCl_2$.	Solids which sublime unchanged at a red heat.

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* These metals are violently attacked at ordinary temperatures, with evolution of much heat.

Symbols of the Metals.	Products of Chlorination.	Properties of Chlorides.
Cu.	(At low temperatures) $CuCl$ and $CuCl_2$.	Solids. $CuCl_2$ at a red heat is reduced to $CuCl$, which, at that temperature, is but slowly volatilized.
Pb, Ag.	$PbCl_2$, $AgCl$.	Solids, fusible below, but not appreciably volatilized at, a dull red heat.
Zn, Cd.	$ZnCl_2$, $CdCl_2$.	Solids, fusible below, and sublimable at, a red heat.
Au, Pt.	(At low temperatures) $AuCl_3$, $PtCl_4$.	Solids, which at certain temperatures below redness are reduced to $AuCl$, $PtCl_2$. These, at a red heat, are reduced to metals.

These data can be advantageously discounted in the analysis of alloys and of mixed metallic sulphides.

303. Halogens.—Iodine when treated with chlorine is converted first into ICl, and then into ICl_3, both solids. The first distils undecomposed at 101°, the second, when heated, is converted into a dissociated vapour of $ICl+Cl_2$. The two chlorides when treated with water behave as if they were mixtures of iodine and a chloride ICl_3, easily acting on water according to equation $ICl_3+5H_2O=5HCl+IO_3H+2H_2O$.

304. Water.—Halogen-water when kept in the dark undergoes no chemical change. Bromine and iodine-water are also not affected, it seems, in the light. But *chlorine-water*, when exposed to daylight, is gradually decomposed, with formation of hydrochloric acid and free oxygen. Chlorine (bromine) when heated to redness with steam is, partially at least, converted into hydride, with evolution of oxygen; iodine, under these circumstances, remains unchanged.

305. *Solutions of strongly* **basic hydrates.**—Solutions of potash, soda, baryta, etc. (also suspensions of oxide of silver in water), readily act on chlorine, iodine, or bromine, with formation of *haloid* R′X, and *halogenate* (RXO or RXO_3, or both).

306. Ammonia.—Chlorine or bromine when added to an *excess* of aqueous ammonia is readily converted into *haloid* of *ammonium*, with evolution of *nitrogen*. The action of an *excess* of chlorine or bromine on ammonia (or NH_4Cl, NH_4Br) gives rise to the formation of *highly explosive* liquids ('*chloride*,' '*bromide*' of nitrogen). *Iodine* when treated even with an *excess of ammonia* is converted, partly into 'iodide of nitrogen,' a black, highly explosive precipitate of varying composition, partly into iodide of ammonium.

307. Reducing agents.—The free halogens, when added to the aqueous solutions (or mixtures with water) of certain substances, act as halogenizing or *indirectly oxidizing* agents; the halogen in the latter case being invariably converted into haloid. Thus, for instance, by the joint action of halogen and water,

(*a.*) Phosphorus is converted into phosphorous or phosphoric acid (PO_3H_3 or PO_4H_3);

(*b.*) *Sulphurous acid* or alkaline *sulphite*, into sulphuric acid or sulphate;

(*c.*) *Arsenious acid* As_2O_3, into arsenic acid As_2O_5.

In cases (*b.*) and (*c.*) the oxidation is complete, if there is enough of alkali present to convert the whole of the acids ultimately formed into normal salts.

(*d.*) *Stannous chloride* is more or less completely converted into *stannic* haloid;

(*e.*) *Mercurous salts* (by an excess of chlorine or bromine at least): into mercuric salts;

(*f.*) Solutions of *cuprous* and *ferrous salts* are, by the action of chlorine or bromine, converted into *cupric* and *ferric* salts respectively. These two oxidations cannot be effected by *iodine;* on the contrary, ferric and cupric salts, when treated with hydriodic acid or alkaline iodides, are *reduced* to ferrous and cuprous salts, with liberation of *iodine*.

308. *Reactions available for the detection of free Halogen,* i.e. *of Cl_2, Br_2, I_2.*

Supposing each of the three substances Cl_2, Br_2, I_2, to be given for itself in the form of a solution in either pure water or in a solution of mineral acids or salts, and,

Bromine and *iodine* are easily distinguished from each other, and from chlorine, by means of *chloroform*, which is not visibly affected by chlorine, while, when shaken with solutions of the other two, it absorbs those and exhibits characteristic intense colours. (See § 297.) *Bromine* and *chlorine*, in opposition to iodine, are characterized by their power of dissolving *gold leaf* as Au(Cl_3 or Br_3), of which the least trace can be detected by means of stannoso-stannic chloride, as shown in § 73; and by their property of readily decolorizing *indigo-solution* in the cold.* A specific reagent for *iodine* is a solution of starch, which, when added to ever so dilute a solution of free iodine produces an intense *blue colour*. This test is the more delicate the lower the temperature. At some temperature below 100° the colour disappears, but it *may* re-appear on cooling. To exhaustively examine a solution for Cl_2, Br_2, and I_2, the best method probably is, first to eliminate the I_2 and Br_2 by means of *chloroform*, and then, after having added, if necessary, enough of water to render any hydrochloric acid non-volatile, to expel the chlorine by distillation or by means of a current of air passed through the liquid in the cold, and to collect and condense the volatilized chlorine in zinc and water as $ZnCl_2$, which, of course, has to be identified. Methods for this purpose will be given presently. From their solution in chloroform, bromine and chlorine can be re-extracted by shaking the solution with water, zinc and a drop of sulphuric acid, when the halogen passes into the aqueous part as $Zn\,X_2$, which can be examined according to § 315. * *Traces of chlorine* (or bromine) can be detected by means of a solution of iodide of potassium, from which either halogen eliminates free iodine, of which the least trace can be detected by means of starch-solution.

309.—II. *The Hydrides HCl, HBr, HI,*

are colourless gases, heavier than air, which, when brought in contact with *moist* air, form dense clouds of hydrates. They are all three eagerly and abundantly dissolved by water, with evolution of much heat. One gramme of water, when saturated with excess of chloride of hydrogen at 15°, and under a partial pressure of 760 mm., absorbs 0·747 grammes of the gas. A solution of halogen hydride in water is colourless and heavier than water itself, the specific gravity of a solution $HX+yH_2O$ being the greater, the greater X and the greater y. The solution when boiled down in contact with its own vapour behaves like a mixture of water with, or an absorption of hydride in, a *definite* (mixed) *hydrate* $HX.nH_2O$, boiling without apparent decomposition at some temperature *above* 100°; n varies slightly with the atmospheric pressure; in case of hydrochloric acid ($X=Cl$) (at any pressure about 760 mm.) it is very nearly $=8$.

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* In applying *these* tests we must not forget that they are not so much tests for the two halogens as tests for a large class of oxidizing agents which happens to include these two species.

The hydrides are strong *monobasic acids*, they readily unite with all metallic bases, forming water and

III. *Metallic Haloids.*

310. Chlorides.—Of the vast number of metallic chlorides a comparatively small number are liquids or very easily fusible solids, which are so volatile that they can be distilled from out of glass retorts; but the majority are *solids*, which, when gradually heated, for themselves, generally melt only at some temperature about dull redness, and at certain higher temperatures, which as a rule lie about or above a bright red heat, are volatilized, more or less readily, most of them without decomposition. Metallic **bromides** generally are similar to the corresponding chlorides, while the **iodides** frequently exhibit a peculiar character of their own. Most metallic haloids, when exposed to a red heat in presence of vapour of water, are decomposed, partially at least, with formation of oxide or oxy-haloid, and halogen-hydride (in case of the bromides and chlorides), or halogen (in case of the iodides). The haloids of mercury and silver are perhaps the only haloids not liable to such decomposition. With regard to their behaviour to liquid water, metallic haloids may be divided into (1.) such which by the action of water are decomposed, with formation of halogen-hydride and metallic oxide (ex. $AsCl_3$), or some insoluble metallic oxychloride (ex. $SbCl_3$, $BiCl_3$); (2.) such which, if not absolutely insoluble, are dissolved, however sparingly, without decomposition. Most haloids belong to the second class and are readily soluble in water. Of the exceptions the most important are included in the following table.

311. *Table showing the solubilities of certain Chlorides as compared with the corresponding Bromides and Iodides.*

Name of Metal. General formula of Salts.	Chloride.	Bromide.	Iodide.
Cuprosum, CuX.	Almost insoluble in H_2O and in dil. H_2SO_4; soluble in NH_3- HCl- NaCl- solutions.	Almost insoluble in water; soluble in ammonia.	Insoluble in H_2O; sparingly soluble in HCl; soluble in (NH_4 salt + NH_3.)
Cupricum, CuX_2	Soluble in water.		Does not exist.
Lead, PbX_2.	Soluble in 135 parts of cold H_2O, easily in hot H_2O.	Sparingly soluble in even hot H_2O.	Soluble in 1200 parts of cold, and in 120 of hot H_2O.
Mercurosum, HgX.	Insoluble in water.		Very slightly soluble in H_2O.
Mercuricum, HgX_2.	Soluble in 18 parts of cold H_2O. More easily soluble in alcohol.	Soluble in 250 parts of cold H_2O.	Insoluble in water; soluble in alcohol; soluble in solution of iodide of potassium.
Palladium, PdX_2.	Soluble in H_2O.	Insoluble in H_2O; soluble in solutions of chlorides.	Insoluble in H_2O; do. in dil. acids: slightly soluble in solutions of certain chlorides.
Platinosum, PtX_2.	Insoluble in water.		
Platinicum, PtX_4.	Soluble in water.		Insoluble in water.
Silver, AgX.	Insoluble in water and dilute acids. Easily soluble in ammonia.	Difficultly soluble in ammonia.	Insoluble in ammonia.

312. *Note.*—Besides the relatively insoluble normal haloids mentioned in this table, there are a large number of more or less sparingly soluble oxy-haloids. It is worth noting that the majority of those chlorides which correspond to strongly basic oxides (as K_2O, BaO, etc.) are less soluble in aqueous hydrochloric acid than in water.

Reactions for the detection of Haloids.

313. (*a.*) *In Solids.*

1. * *Concentrated sulphuric acid*, when heated with solid haloids, produces the following effects :—*Chlorides* give off white fumes of HCl only; *bromides:* HBr mixed with SO_2 and brown vapours of Br_2; *iodides:* violet vapours of iodine, SO_2, and little or no HI.

2. * Anhydrous haloids, when mixed with *bichromate* of *potash* and then distilled with excess of *concentrated sulphuric* acid, behave as follows :—*Chlorides* give a distillate consisting of *chlorochromic* acid CrO_2Cl_2, a heavy liquid (resembling bromine in appearance), which when treated with excess of dilute ammonia yields a *yellow* solution of ammonium chromate and chloride. *Bromides* and *iodides* yield free halogen, which when treated with excess of ammonia yields, the Br_2: a *colourless solution* of bromide of ammonium; the I_2: black insoluble iodide of nitrogen. This reaction is available for the detection of *chloride* in presence of *bromide* (but *not* in presence of iodide†), the presence of chromium in the distillate demonstrating that of chloride in the substance; but this evidently is a very weak point in the method.

3. If a *microcosmic salt* bead, previously charged with *oxide of copper*, is fused together at the end of the inner blue cone of an oxidizing blowpipe-flame with a *metallic haloid*, some of the copper volatilizes as haloid, and imparts to the flame an intense colour, which, in the case of chlorine, bromine, iodine, is *blue* throughout, blue on the whole but green at the edges of the flame, *pure green*, respectively.

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* Does not hold for the haloids of silver and mercury. Test No. 2 is probably available only for the haloids of those metals which form sulphates of great stability.

† Not even, if *caustic potash* is substituted for the ammonia.

314. (*b.*) *In Solutions.*

4. *Nitrate of silver*, from neutral or acid solutions of *haloids*, precipitates the halogen completely in the form of *haloid of silver.* The precipitate is at first milky, but on shaking becomes curdy and settles very readily, so that it can easily be washed by decantation. Haloid of silver is as good as absolutely insoluble in water (hot or cold), and in cold dilute nitric or sulphuric acid, and in solutions of most ordinary metallic salts. It is scarcely affected when *boiled* with *dilute* nitric or sulphuric acid. But it is appreciably soluble in solutions of hydrohalogenic acid (HX) and of haloids generally, and more or less readily soluble in alkaline *thiosulphates* and cyanides. When heated to dull redness it melts without decomposition or volatilization into a clear colourless or yellowish fluid, which, on cooling, solidifies into a horny mass ('horn-silver'). When fused with alkaline carbonate it is decomposed, with formation of silver, oxygen, and alkaline haloid. When treated with *zinc*, *water*, and a little sulphuric acid, it is reduced to metal, with formation of a solution of *haloid of zinc* ZnX_2. When recently precipitated, *chloride* of silver is *white*, the *bromide* yellowish white, the *iodide* decidedly yellow. The three precipitates when exposed to daylight suffer partial reduction, and consequently get discoloured. The *chloride* is easily soluble, the *bromide* difficultly soluble, and the iodide almost insoluble in *aqueous ammonia.* If the ammoniacal solution is acidified with nitric acid the dissolved haloid (AgCl,AgBr) is re-precipitated. The haloids of silver, although all three practically *insoluble* in water and dilute nitrates, are not insoluble to exactly the same extent. If a mixed solution of chloride, bromide, and iodide is precipitated, with continuous agitation, by gradual addition of nitrate of silver, the iodine goes down first, the bromine next, the chlorine last. Although it is not possible in this way to effect anything like a quantitative separation, the method of fractional precipitation may serve for, so to say, concentrating small quantities

of iodide or bromide diffused through large quantities of chloride, and *vice versa.*

5. *Sulphate of copper*, when added to a neutral or moderately acid solution of an *iodide*, gives a dirty white precipitate of *cuprous iodide* CuI, and a solution containing *free iodine.* If sulphurous acid is added to the mixture in sufficient quantity to reduce the iodine to hydriodic acid (and if necessary an additional quantity of copper salt), the whole of the iodine is converted into and almost completely precipitated as cuprous salt. *Chlorides* and *bromides*, in sufficiently dilute acid liquids at least, do not under these circumstances show any visible tendency of passing into *cuprous* compounds, and consequently, if present, remain dissolved. (Comp. § 311.)*

6. *Nitrate of palladium* is a most delicate and, in presence of a moderate quantity of chloride, also a *characteristic* precipitant for *iodide.* The black precipitate PdI_2 is insoluble in dilute acids and little soluble in chlorides. In absence of *chlorides*, *bromides* also are precipitated by the reagent.

7. *Dilute mineral acid*, when added to a dilute solution of haloid, liberates HX, which in the case of chlorides is stable in presence of air, while the two other hydrides absorb oxygen, the bromide slowly, the iodide more rapidly, with elimination of free halogen. If the acid (or the original neutral) solutions are mixed with

8. *Chlorine-water*, then, in the case of chloride, there is no change, while the two other haloids are decomposed with elimination of free halogen. The *iodine* sometimes separates out as a black heavy precipitate, but as a rule it remains dissolved, producing a brown, yellow, or, if present in *very* small quantity, a colourless solution. The least trace of iodine thus liberated can be detected by means of *chloroform* or *starch solution.* (Comp. §§ 297 and 308.) The *bromine* always remains dissolved and, if present in ap-

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*** According to *Mohr*, a solution of cuprous chloride in hydrochloric acid is a better precipitant for iodide than ordinary sulphate mixed with sulphurous acid.**

preciable quantity, imparts to the solution a colour similar to, but far less intense than, that produced by iodine. Traces of bromine can be detected (and Br_2 generally be distinguished from I_2) by means of chloroform. (Comp. § 297.) If the liberated *halogens* (Br_2, I_2) are treated with an excess of *chlorine*, then the *bromine* remains substantially unchanged, but the *iodine* is converted into *iodic acid*, which does *not* colour starch or chloroform, and is not dissolved out by this liquid. The liberation of *iodine*, from acid solutions of iodides, may also be effected by

9. *Nitrous acid*,* which reagent offers this advantage over free chlorine, that an excess of it does not affect the liberated halogen, and that it does *not* decompose *pure* bromides at least. In presence of chlorides, bromides *are* decomposed, with liberation of bromine.

315. *Examination of a Solution of Salts for Haloids.*

Given a solution of salts in water or dilute mineral acid, which is free from oxygen-acids of iodine and bromine, from cyanides, sulphides, thiosulphates and polythionates, and—however complex its composition may be otherwise—all that may be present in it in the shape of *haloid* can be eliminated completely by adding a slight excess of nitrate of silver, and, after removing the mother liquor, extracting from the precipitate what is soluble in dilute (say 10°/₀) nitric acid and washing the undissolved portion. This portion can contain nothing but *haloid of silver*.

To analyse such haloid, first decompose it with zinc, water, and a drop of sulphuric acid (see § 314, under 4), and remove the silver by filtration. Supposing now—as we will, to avoid circumlocution—the solution actually contained the three halogens as zinc salts, then the presence of *iodine* is easily demonstrated by adding, to a small portion of the liquid, first dilute sulphuric acid and starch (or chloroform), and then a quantity of nitrous acid or chlorine water, which must be adjusted so as to be presumably *insufficient* to liberate the whole of the iodine. If this precaution be observed, any locally formed free bromine is ultimately replaced by iodine, and the test will not fail. In order now to test for bromide, one method is, first to liberate the iodine with nitrous acid in presence of starch, then to add chlorine-water until the blue colour has disappeared, *i.e.* until the whole of the iodine has been converted into iodic acid, and lastly by shaking with chloroform to collect and detect the free *bromine.* This method, however, will not succeed if the bromide was associated with much iodide. In this case it is better first to remove the iodine (from part of the original zinc-solution) by means of *sulphate of copper* and sulphurous acid, to allow the precipitate to settle, to filter, to expel from the filtrate the sulphurous acid by boiling, then to eliminate the copper by means of metallic zinc, and lastly to test for *bromine* by means of chlorine-water and chloroform—in a part of the liquid. The rest might be evaporated to dryness, and in the residue the *chloride* searched for by distillation with *chromate* and sulphuric acid (§ 313, 2). But it is far better to remove the bromide (and perhaps part of the chloride) by fractional precipitation with nitrate of silver, and in the filtrate—after having demonstrated the presence of haloid—to prove the *absence* of bromide and iodide. This method succeeds very easily if the chloride predominates largely; if it does not, the following *modus operandi* may be adopted:—From the original haloid solution—or after elimination of the iodide—precipitate *all* the haloid by means of nitrate of silver. Wash the precipitate by decantation with cold water, then digest it for some hours with say $\frac{1}{100}$th of its equivalent of iodide of potassium, and filter. If the filtrate contains haloid, *not* bromide or *iodide*, it must necessarily contain chloride. If the original solution contained no other metallic bases than alkalis, alkaline earths, alumina, zinc or cadmium oxides, and was free from a certain class of acids which includes nitrous and sulphurous, besides fulfilling the conditions enumerated at the outset, then the three halogens may be searched for at once without first letting them pass through the condition of silver-salt.

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* *i.e.* in practice, by addition of a solution of N_2O_3 in concentrated sulphuric acid, or by the successive addition of *nitrite of potash* and dilute nitric or sulphuric acid.

IV. *Halogen-oxides and Hydroxides, and their Salts.*

316. The following oxides and hydroxides of halogen are with certainty known to exist:—

Cl_2O	Cl_2O_3	Cl_2O_4	I_2O_5	
($HClO$?)	($HClO_2$?)	. . . .	$HClO_3$	$HClO_4$
			($HBrO_3$?)	
			HIO_3	HIO_4xH_2O

All these compounds, except Cl_2O_4*, are acids or acid-anhydrides. The chlorine and bromine acids are all monobasic; but the acids HIO_3 and HIO_4 represent each of them only one of the several series of salts which the respective oxide (I_2O_5 or I_2O_7) is capable of forming.

317. Of the alkaline (K- or Na-) salts of the acids under consideration, *most of* those which correspond to the formula RXO_y, when heated to redness, are completely reduced to haloids (RX) with evolution of oxygen (O_y). Under the same circumstances, *all the silver-salts* of these acids, without exception, leave residues which contain the whole of the haloid of silver originally present (potentially) in the salt.

All the chlorine acids enumerated, except perchloric $HClO_4$, when treated as aqueous solutions with excess of *sulphurous acid*, are readily *reduced*, especially on heating, to *hydrochloric acid.* Solutions of *iodic*, *bromic*, and *periodic* acids, on gradual addition of sulphurous acid, give first *free halogen*, which, by an excess of the reagent, is converted into hydride. Thus, for instance, IO_3H is reduced, first to free iodine, ultimately to hydriodic acid.

Oxygen Acids of Chlorine.

318. Hypochlorous acid.—The anhydride Cl_2O is a yellow gas of 3·0 spec. grav. (air=1), possessing a strong peculiar odour. It is very unstable, being readily decomposed —on exposure to sunlight, or even local application of heat—into chlorine and oxygen, with *evolution* of *heat.* This decomposition, under certain circumstances, takes place suddenly, with explosive violence. The gas Cl_2O is absorbed by water; the solution, if sufficiently strong, exhibits a yellow colour. When left to itself it gradually suffers decomposition, with formation of chloric acid, chlorine, and oxygen. The same decomposition takes place more readily on boiling. The solution when mixed with solutions of basic hydrates (KHO, BaO_2H_2, etc.) is converted into one of *hypochlorite* ($RClO$; $R=K$, $Ba_{\frac{1}{2}}$, etc.), (a class of salts which are not known as yet in the *dry state*). Hence the solution of Cl_2O in water is, so far at least, virtually equivalent to one of $HClO$. A dilute solution of what really seems to be $HClO$ is obtained by passing chlorine through a suspension of carbonate of lime in water. The mixture, when distilled, yields a distillate, which, even after repeated distillation, gives no precipitate with nitrate of silver.[*] This solution (as also the absorption of Cl_2O in water) bleaches *indigo* like chlorine-water, from which it can, however, be distinguished[†] by its behaviour, on being shaken up, for a sufficient time, with mercury. Dissolved Cl_2 is completely converted into *calomel*, which is insoluble in hydrochloric acid; Cl_2O is also completely decomposed, but with formation of a mercuric oxychloride, which dissolves in hydrochloric acid as *corrosive sublimate* $HgCl_2$.

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* This oxide may be looked upon as being a mixed anhydride of $HClO_2$ and $HClO_3$.

If solutions of fixed alkaline carbonates or hydrates, or of the hydrates of the alkaline earths, or the same substances in the dry state, are treated, *in the cold*, with free chlorine, the gas is largely absorbed, with formation of substances of the composition $R'_2O.Cl_2$, which in the case of mono-acid bases are mixtures, but in the case of the di-acid ones seem to be compounds, of chlorides and hypochlorites. Ex.: $K_2O.Cl_2$

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[*] But if the mixture is rendered alkaline by addition of potash, the hypochlorite suffers deoxidation, with formation of a black precipitate, containing an unstable *peroxide of silver.*

[†] According to *Wolters.*

$= KCl + KClO$; $Ca''O.Cl_2 = Cl\text{-}Ca\text{-}(ClO)$. Ordinary bleaching-powder is essentially a mixture of this compound, with more or less of hydrate and carbonate of lime. These substances, when treated with excess of mineral acid, behave as if they *were* $Base + Cl_2$, but when distilled with much water and *less* acid than is required to saturate the base of the hypochlorite, yield distillates of $HClO$.

319. Chlorous acid $HClO_2$ is not known. The anhydride Cl_2O_3 forms a yellowish green gas of 4·1 spec. grav. (air=1). When heated to about 57°, it is decomposed, with explosion, into $Cl_2 + \frac{3}{2}O_2$. It is soluble in water (at 14° and 760 mm. in 20 parts), forming a greenish-yellow liquid, which stains the skin. It bleaches indigo in the cold. The solution acts but sluggishly even on *caustic* alkalies, and not at all on carbonates. The lead salt and the silver salt are sparingly soluble in water.

Aqueous alkaline hypochlorites and chlorites are decomposed on boiling, with formation of chlorates and chlorides Ex. $3KClO = 2KCl + KClO_3$. *If, previous to the application of heat, a small quantity of sesquioxide of cobalt is produced within the liquid (by addition of a drop of cobalt salt), then a part at least of the dissolved salt breaks up into chloride and oxygen.*

320. Chloric acid $HClO_3$ is a syrupy liquid, miscible in all proportions with water. The oxide Cl_2O_5 is not known. The acid, although far more stable than $HClO$ and $HClO_2$, when heated for itself, or in the form of an aqueous solution, breaks up into perchloric acid, chlorine, oxygen, and water. A solution of the acid (or of a chlorate mixed with dilute sulphuric acid) does not, *in the cold*, destroy the colour of *indigo solution*, but it does so if acting conjointly with a quantity of sulphurous acid *insufficient* to remove the *whole* of the O_3 from the $HClO_3$. All normal chlorates are soluble in water; the least soluble of the class are those of potassium and rubidium. (See § 254.) *Solid chlorates* are violently acted upon by *concentrated sulphuric acid* with formation of perchloric acid and of the oxide Cl_2O_4, of which a part remains dissolved, imparting to the mixture a deep *yellow* colour.

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* Probably generally true, but proved only for a solution of bleaching powder.*

All these oxygen-acids of chlorine—and also their salts when used conjointly with free mineral acids—are strong oxidizing agents. On the chlorine-reducers named in § 307 they act, substantially, like free chlorine, *i.e.*, they act as if they consisted of active oxygen + free chlorine.

321. **Perchloric acid** $HClO_4$ is a colourless, very volatile liquid of little stability. When dropped on wood or other combustible matter, it is instantaneously reduced (and the combustible oxidized) with violent explosion. It eagerly combines with water, with considerable evolution of heat. $HClO_4.H_2O$ is a crystalline solid, more stable than the acid itself. The crystals, when mixed with the proper quantity of water, are converted into an oily liquid which very much resembles oil of vitriol, not merely in appearance, but also in its action on wood, sugar, starch, which it decomposes (as oil of vitriol does) with formation of charcoal. If exactly composed according to the formula $HClO_4 + \frac{15}{7} H_2O$, it distils at 203°, without change of composition. In this form, or when given in the form of weaker hydrates, perchloric acid possesses a high degree of stability.

Dilute solutions of perchloric acid (or of perchlorates mixed with sulphuric acid) do *not* bleach indigo, nor oxidize sulphurous acid in the least, even on boiling.

Most normal perchlorates are easily soluble in water; the most sparingly soluble of all are the potassium, rubidium, and cæsium salts. (See § 254.)

Solid perchlorates, when treated with *concentrated sulphuric acid* in the cold, dissolve quietly into a *colourless* fluid containing *no* lower chlorine oxide.

322. The **silver salts** of all oxygen acids of chlorine are soluble in water, except the chlorite $AgClO_2$ which dissolves in nitric acid.

Oxygen-Acids of Bromine and Iodine.

323. **Bromic acid** $HBrO_3$ is known only as an aqueous solution which, when heated to 100°, gives off bromine and

oxygen. The aqueous acid reddens litmus and then bleaches it.* By sulphurous acid the BrO_3H is reduced, first to Br_2, then to HBr. **Bromates** $R'BrO_3$ (where R′ = 1 *equiv.* of metal) are most of them soluble in water; the silver, lead, and mercurosum salts are insoluble, or nearly so, in water. *Solid bromates*, when treated with concentrated *sulphuric acid*, give off bromine and oxygen; with concentrated *hydrochloric* acid they yield a yellow solution containing bromide of chlorine; with *hydriodic acid:* bromide of iodine. **Solutions of bromates** when mixed with dilute *sulphuric acid* are decomposed with elimination of $HBrO_3$ (*vide* supra). When mixed with *nitrate of silver* they give a white precipitate $AgBrO_3$, which is sparingly soluble in water and in cold dilute nitric acid, but more readily soluble in ammonia. Concentrated sulphuric acid decomposes the silver-salt as it does other bromates.

324. *Perbromic acid* $HBrO_4$ is said (by *Kämmerer*) to be formed by the action of bromine on perchloric acid. (?)

325. Iodic acid $I_2O_5.xH_2O$.—The hydrate HIO_3 (prepared by oxidizing iodine by means of the strongest nitric acid in the heat, and evaporating to dryness) is a white crystalline solid, easily soluble in pure water, but far less soluble in dilute nitric acid, dilute sulphuric acid, or alcohol. At 170° it loses its water and leaves the anhydride I_2O_5, which at a higher temperature breaks up into its elements. An aqueous **solution** of the **acid**, on gradual addition of *sulphurous acid*, is reduced, first to halogen, then to hydride. Iodic and *hydriodic acids*, when mixed as aqueous solutions, decompose each other completely into *iodine* and water: $HIO_3 + 5HI = 3I_2 + 3H_2O$. Iodic acid [and any iodate], when boiled with strong *hydrochloric acid*, is decomposed completely, with formation of free chlorine, terchloride of iodine [and metallic chloride]; thus: $I_2O_5 + 10HCl = 2ICl_3 + 2Cl_2 + 5H_2O$. Aqueous iodic acid readily saturates bases, with formation of *iodates.*

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* Hence it appears that bromic is less stable than even chloric acid, and, *a fortiori*, far less stable than iodic acid. This is quite in accordance with the results of Thomsen's thermochemical investigations, which show that, in affinity to oxygen, iodine exceeds chlorine, and chlorine exceeds bromine.

326. Metallic iodates.—There are two classes of iodates: 1stly, '*normal iodates,*' $R'_2OI_2O_5$, and 2dly, '*acid iodates,*' $R'_2O.I_2O_5.xI_2O_5$ (where R' means one *equivalent* of metal). Most metallic iodates are insoluble or difficultly soluble in water. Even the alkaline salts are rather sparingly soluble. Thus, for instance, the salts

	$K_2O.I_2O_5$	$K_2O.2I_2O_5$	$K_2O.3I_2O_5$	
dissolve, at 15°, in	15	75	25	parts of

water respectively. All metallic iodates are completely decomposed at a red heat; the potassium salts exactly according to the equation $KIO_3.xI_2O_5 = KI + O_{(3+5x)} + xI_2$; the *sodium* salts into iodine, oxygen, and a residue of the empirical composition $Na_8I_6O_3$, which behaves to reagents as if it was $6NaI + Na_2O_3$ (comp. § 252); the iodates of di- or poly-valent metals: into oxygen, iodine, and a residue consisting of pure oxide, or a mixture of iodide and oxide, or basic periodate. The baryta salt $BaOI_2O_5$, for instance, is decomposed thus: $5Ba(IO_3)_2 = 4I_2 + 9O_2 + I_2O_7.5BaO$.

Behaviour to Reagents of

327. Solid iodates.—Concentrated sulphuric acid liberates the acid, which in itself is stable, but, in presence of organic matter or other reducing agents, yields violet vapours of iodine. (Comp. § 323.)

328. Solutions of iodates.—*Nitrate of silver* (from neutral or nitric solutions) precipitates a white silver salt, which always is $AgIO_3$, whatever may have been the formula of the original salt. The precipitate is almost insoluble in water and in cold dilute nitric acid, but is readily soluble in ammonia. If the ammonia solution is mixed with *sulphite* of ammonia, the iodate is reduced to, and precipitated as, iodide AgI. *Chloride of barium* gives a white crystalline precipitate $BaO.I_2O_5.H_2O$, nearly insoluble in water and difficultly soluble in dilute nitric acid, but dissolved, with decomposition, by hydrochloric acid. Dilute *sulphuric acid* produces a liquid which exhibits the reactions of the free aqueous acid. (See § 325.)

329. Periodic acid.—The hydrate $I_2O_7.5H_2O$ forms colourless crystals, which lose no weight at 100°. At 130°–136° it melts, but at the same time begins to break up into water, oxygen, and *iodic* anhydride I_2O_5, which at temperatures below 200° remains undecomposed. The anhydride I_2O_7 cannot be obtained. The acid readily dissolves in water, forming a solution, which shows all the properties of a strong aqueous acid, and to *sulphurous* or *hydriodic acid* behaves exactly like one of iodic acid.

330. Periodates.—Periodic acid forms a great variety of metallic salts, the quantity I_2O_7 being capable of uniting with $(1, 2, 3, 4, 5) \times (R'_2O \text{ or } R''O)$, with formation of definite salts, of which those with less than 5 equivalents of base often contain the elements of water in *atomic* combination. The following is a list of the formulæ of the best-known periodates of potassium, sodium, silver, and barium :—

(1.) *Monobasic* ('normal') salts: KIO_4; $NaIO_4$; $AgIO_4$.

(2.) *Dibasic* salts $I_2O_7.2R_2O$: $K_4I_2O_9$; $K_4I_2O_9.9H_2O$; $Na_4I_2O_9.3H_2O$; $Ag_4I_2O_9.3H_2O$; $Ag_4I_2O_9.H_2O$; $Ba_2I_2O_9$; $Ba_2I_2O_9.6H_2O$; $Ba_2I_2O_9.7H_2O$.

(3.) *Pentabasic* salts R_5IO_6 or $I_2O_7.5R_2O$: Na_5IO_6(?); Ag_5IO_6; $Ba_5I_2O_{12}$.

331. Action of Heat.—The pentabarytic salt $Ba_5I_2O_{12}$ is stable at a red heat; all other periodates are decomposed on ignition, with evolution of oxygen. The normal periodates RIO_4 of potassium, sodium, silver, when kept at 250°-300°, 250°-300°, 175° respectively, are reduced to *iodates* RIO_3 which at higher temperatures break up as stated in § 326 and § 317. With exception of certain of the salts just named, and of the silver salts generally, **all periodates** when ignited give off *iodine* (besides oxygen), and some of them leave almost pure oxide (ex. the MgO and NiO salts); others, a mixture of oxide and iodide (ex. the Pb-, Cd-, Cu-, salts). The mercury salts yield metal, iodine and oxygen. The ammonium salts are decomposed, with detonation into iodine, oxygen, nitrogen and water. Of the *basic periodates* $IO_4R'.xR_2O$, the silver salts are the only ones which after ignition leave residues free from oxygen. The less basic baryta salts leave *pentabarytic* salt; the dibasic potash and soda salts leave residues (of $R'I_2O$ or, at lower temperatures, of $R'_4I_2O_3$), the constitution of which is little understood.

The sodium-compound* $Na_4I_2O_3$ is probably $2NaI+Na_2O_3$; its solution in water behaves to reagents as if it contained the as yet unknown salt Na_5IO_6.

332. Solubility relations.—Periodates as a rule are sparingly soluble or insoluble in water but soluble in dilute nitric acid. Even the alkaline periodates are not by any means readily soluble. The disodic salt $I_2O_7.2Na_2O+3H_2O$ (which is obtained as a precipitate when chlorine is passed into a mixed solution of iodate and hydrate of soda) is almost insoluble in water; the normal potash salt KIO_4 dissolves in no less than 300 parts of cold water. No aqueous periodate is neutral to litmus; the 'normal' ones exhibit an acid, the alkaline dibasic ones an alkaline reaction.

333. Reactions of solutions of alkaline periodates.—*Dilute sulphuric acid* liberates periodic acid (*vide* supra). A suspension in water of a dibasic salt, when treated, at a boiling heat, with chlorine, yields normal *periodate*, chlorate, and chloride,† thus: $3K_4I_2O_9+6Cl=6KIO_4+KClO_3+5KCl$. *Iodine*, under similar circumstances, yields *iodate*, both with the Na- and the K- salt: $Na_4I_2O_9+I_2=3NaIO_3+NaI$. When a solution of normal alkaline periodate is mixed with *iodide of potassium*, *iodine* separates out as a precipitate, which however, on heating, quickly dissolves, with formation of a colourless solution of *iodate* (and iodide), in accordance with equation $3KIO_4+KI=4KIO_3$ (*Philipp*, Jahresb. f. 1869, p. 224). A solution which, if necessary, has been neutralized or slightly acidified with nitric acid, when mixed with *nitrate of silver*, gives a precipitate, which looks brown at first, but black after settling, and then consists of $I_2O_7.5Ag_2O$. This or any other basic periodate of silver, when dissolved in nitric acid, yields, on evaporation, orange-red crystals of $I_2O_7.Ag_2O$, which salt, when treated with water, breaks up into $I_2O_7.2Ag_2O$ and free acid.

Examination of an Aqueous Solution of Alkaline Salts for Halogen Acids.

334. We assume the solution to be neutral or alkaline to litmus-paper, because it is only in this case that certain classes of halogenides can co-exist in the same solution. On the other hand, to simplify matters, we altogether ignore *chlorous* and *periodic acids*, and assume cyanogen-acids, sulphides, thiosulphates, polythionates (as also tungstates and certain other rare compounds) to be *absent.*

Before attempting an exhaustive analysis, it is advisable first to subject separate small portions of the solution to the following tests :—

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* The K-compound is not known.

† Holds chiefly for the K-salt; the Na-salt is not so readily attacked.

335. Acidify with dilute sulphuric acid, and note the effect. If (*a*) the liquid becomes yellow or brown, from iodine or bromine liberated, this proves the simultaneous presence in the original liquid of either (iodides, bromides), and certain oxidizing, or of (iodates, bromates) and certain reducing agents; *i.e.* of combinations such as iodate + iodide; iodide + hypochlorite or nitrite; bromate or iodate and sulphite, etc. etc. If necessary, the liberated halogen can be removed by repeated treatment of the mixture with successive small doses of *chloroform*, and [after separation of the latter (*i.e.* of the $CHCl_3+X_2$) by means of a pipette, and the removal of the adhering aqueous portion by means of water] be converted into zinc-salt, and, in this form, be analysed according to § 315. If (*b*) *no* halogen was liberated (or after removal of the halogen by chloroform), test one portion of the solution for (iodic, bromic) acid with sulphurous acid; another for bromic or hypochlorous acid with *indigo in the cold*, and, in case of a negative result, for *chloric acid*, by cautious addition, to the blue liquid, of *sulphurous* acid; a third (if necessary) with chlorine-water for iodides and bromides.

(2.) Add nitrate of silver and, if a precipitate is formed, excess of nitric acid. If the liquid becomes clear, this at once proves the absence of *haloids*, and of considerable quantities of iodates and bromates.

Supposing now, for the sake of generality, these preliminary tests had not proved the absence of any of the acids under consideration, then an *exhaustive analysis* may be attempted in the following manner :—

336. To a portion of the *neutral or alkaline* solution, add a slight excess of nitrate of silver in the cold, and next separate precipitate (P) and liquid (F) by decantation or filtration.

The *precipitate* contains the whole of the *haloid* and the bulk, in general, of the *iodate* and *bromate;* but it may contain besides a very great variety of foreign silver-salts. Of these the majority are easily removed by cold dilute nitric acid.* Supposing this operation to have been performed, and the residue washed, then this residue, even in the most complex case, could contain nothing but (*a*) Ag [Cl, Br, I, (IO_3), (BrO_3)]; (*b*) Ag_2S, AgNC, AgNCS, and the silver-salts of certain complex cyanogen acids. But we have supposed these foreign acids (*b*) to be absent, and consequently can look upon the precipitate as consisting potentially of the salts (*a*) only. In this case a mere examination for the *elements* Br, Cl, I is easy. We need only treat the precipitate with *zinc*, *water* and *sulphuric acid*, and all the halogen (including what was originally halogenate) is obtained ultimately in the form of a solution of *haloid of zinc*, which can be analysed as shown in § 315. The separation from one another of the *radicles* Cl, Br, I, (IO_3) (BrO_3) is not so easy. To test for the *group* $AgXO_3$, dry part of the precipitate and heat it in a sublimation-tube: the oxygen, from the $AgXO_3$, is readily evolved, and can be identified by means of a glowing splinter of wood; or else treat the precipitate with iodide of potassium which dissolves the *iodate*† at any rate, with formation of a solution, which on addition of hydrochloric acid gives *free iodine.* The radicle BrO_3 is easily tested for by heating the precipitate with concentrated sulphuric acid, which decomposes the *bromate*, with evolution of bromine-vapours, while it does not decompose the acids contained in the other four salts. An actual (qualitative) separation of the two radicles $(XO_3)'$ from the radicles X' could *probably* be effected by digestion of the precipitate in cold solutions of successive small quantities of chloride of potassium, which would decompose the *halogenates* (into halogenate of alkali and chloride of silver) without attacking the haloids.‡

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[*] The nitric extract may contain *chlorous acid*, regarding which see § 319.

[†] And no doubt also the bromate; but this has not yet been proved.

[‡] The method, according to a few experiments I have made, seems to work, but I *cannot say* that I have tested it rigorously.—(*W. D.*)

The filtrate F contains all that was present originally of oxygen acids of chlorine,* and, in general, traces of iodic and bromic acids. To analyse it, add, first, enough of sulphuric acid to neutralize the alkali, if present; then excess of sulphurous acid and more nitrate of silver (if necessary); and lastly keep the mixture at a gentle heat for some time. The effect is that all that part of the halogen which is *not* perchloric acid is converted into, and precipitated as, *haloid of silver* along with more or less of sulphite, which however, after decanting off the mother liquor F′, is easily removed by means of warm dilute nitric acid. If the haloid of silver is found on examination to contain *chloride*, the chlorine in it must originally have been $(ClO)'$ or $(ClO_3)'$. To examine the filtrate F′ for *perchlorate*, first expel the excess of sulphurous acid by boiling, next remove the excess of silver by means of sulphuretted hydrogen, and then, after having expelled the excess of this reagent by boiling, test for *chlorine*, which is easily done by saturating the acids present with pure alkaline carbonate, evaporating to dryness, igniting the residue, and then searching for *chloride*. If a positive result is obtained, this indirectly proves the presence, in the liquid F′, of *perchlorate*.

A more direct method (which however presupposes the absence of potash salts, and does not work with small quantities) is—after removal of the sulphide of silver and of the excess of sulphuretted hydrogen—to convert all the acids present into a mixture of *dry sodium salts*, to treat this mixture with *absolute alcohol*, and from the filtered extract to precipitate the perchloric acid by means of an alcoholic solution of *acetate of potash* as $KClO_4$. This salt, of all perchlorates, is most easily identified by its properties.

337. V. *Organic Halogenides*,

from the standpoint of the Analyst, may be classified as follows :—

1. The *hydrochlorates*, hydrobromates, hydriodates of organic *bases proper*, *i.e.* bases such as ethylamine, quinine, etc. These substances,

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* See, however, footnote to § 318.

as aqueous solutions, behave to nitrate of silver like ordinary haloids, and consequently are easily investigated.

2. *Halogenides of acid radicles, e.g.* chloride of acetyl, phosgen, etc. All these, when treated with water, break up into their acids and *hydro-halogenic acid*, which is easily analysed, resp. identified.

3. *Haloids of alcohol-radicles.*—These haloids are all soluble in alcohol, and in many cases the alcoholic solution, when mixed with alcoholic nitrate of silver, gives a precipitate containing a part of the halogen as haloid of silver. A far more general and thoroughgoing method of analysis, however, is to treat the alcoholic solution in a close vessel (*e.g.* in a sealed-up glass tube) with excess of *alcoholate of sodium** at 100°, when, in general, the whole of the halogen is after some time eliminated as *haloid of sodium*, which can be identified or analysed in the usual way.

4. *Chloro-, bromo-, iodo-substitution products, i.e.* halogen compounds, not haloids proper. From a comparatively small class of bodies falling under this head, the halogen can be extracted by treating them with water and sodium amalgam, when the halogen passes into the state of haloid of sodium. This applies, for instance, to the bromo-substitution products of succinic and of some other acids. But a much more general method, which in fact applies to all organic halogen-compounds without exception, is to *burn* the substance in a combustion-tube with *caustic lime.* If matters be arranged so that the volatile products of combustion cannot escape into the air without first having passed through a column of red-hot lime, the whole of the halogen remains in the residue (along with more or less charcoal) as normal or basic *haloid of calcium.*

338. *Disintegration of Halogen-salts insoluble in water.*

1. Of *haloids* and halogenates insoluble in water, many dissolve in dilute nitric acid. If the solution was prepared in the cold, it can, *in general*, be assumed to contain the original halogen-radicles unchanged. If heat has to be applied, it is as well to add some nitrate of silver from the first, to prevent volatilization of halogen.

2. Insoluble *haloids and oxy-haloids* of metals of the *copper* and *arsenic* groups can, in general, be decomposed by being treated with *zinc*, *water* and a few drops of sulphuric acid, when the bases are reduced to the metallic state, while

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* Solution of sodium in absolute alcohol.

the halogen passes into solution as zinc salt. Or else, by prolonged treatment of a suspension of the finely divided compound in water with *sulphuretted hydrogen*, when the metals are converted into insoluble sulphides, while the halogen is eliminated as a solution of hydride. Neither of these methods works satisfactorily with

3. *Mercuric iodide*, which, however, according to *Meusel* (*Jahresb. f.* 1870, page 943), can be decomposed with quantitative exactitude, by dissolving it in the least quantity of a concentrated solution of *thiosulphate of soda*,* and then adding an excess of *sulphide of ammonium;* the mercury is completely precipitated as sulphide, while the iodine remains dissolved as *iodide.* The filtrate is evaporated with ammonia, to expel part of the sulphur, the residue mixed with caustic soda, evaporated to dryness, and heated in a platinum basin to destroy the polythionates. The ignited mass is dissolved in water and distilled with ferric chloride, when all the iodine passes over as such.

4. Insoluble oxy-haloids of the *iron*, *barium*, *magnesium* (and copper) groups of metals can, as a rule, be at least partially decomposed by boiling the finely divided substances with aqueous carbonate of potash, and the halogen thus be extracted as alkaline haloid. A perfectly *complete* decomposition in all these cases (except in that of HgI_2 or HgI) can be effected by *fusion* of the substance with *excess of alkaline carbonate.* The fused mass contains the halogen as RX, the base as carbonate or oxide or (in case of silver) as metal.

The methods of disintegration given under 2, 3, 4, will as a rule work also—more or less satisfactorily—with *halogenates*, but obviously the solutions obtained are in many cases available only for the purposes of an *ultimate* analysis. Nobody, of course, would think of searching, say, for iodate or bromate in a solution which had been treated with sulphuretted hydrogen in presence of free acid, or in a substance which had been exposed to a red heat; but even if the halogen-radicles were extracted, say, by boiling with a solution of alkaline carbonate, we cannot be too slow in assuming them *all* to have remained what they originally were.

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* The mercurous salt when thus treated probably breaks up into Hg, and a solution of HgI_2.

II. SULPHUR, SELENIUM, TELLURIUM.

A. Sulphur.

339. I.—'*Free Sulphur*'

exists in a variety of allotropic modifications, *i.e.* there are a variety of substances which altogether consist of *this* element. Of these the following are the more important:—

(1.) **Octahedral sulphur** S_α occurs in nature in the shape of lemon-yellow, translucent, octahedral crystals belonging to the right prismatic system, of the spec. grav. 2·05. When gradually heated it begins to melt at 114°.5, and at 120° is changed into a thin pale-yellow liquid, which, however, *now* consists of

(2.) **Prismatic sulphur** S_β, which, by allowing the liquid to partially solidify, and pouring off the liquid portion, can be obtained in isolated *monoclinic prisms* of the spec. grav. 1·98.

(3.) **Plastic sulphur**, S_γ. When melted S_β is gradually heated further, it becomes more and more viscid, passing gradually into S_γ. At 200°-250° the mass is stiff like treacle; at higher temperatures it again becomes more fluid; and if now suddenly cooled down (by being poured into cold water), it is obtained as a *plastic* yellowish-brown mass of the spec. grav. 1·95; *i.e.* as S_γ.

S_α and S_β are readily soluble in *bisulphide of carbon*; the solution, on evaporation, deposits octahedra of S_α. S_γ does *not* dissolve in the bisulphide. S_β and S_γ, if left to themselves at the ordinary temperature, gradually pass into the condition of S_α. Ordinary 'roll-sulphur' and 'flowers of sulphur' consist, generally, of a mixture of S_α, S_β, and, if recently made, more or less of S_γ. The finely divided white sulphur ('*lac sulphuris*'), which is obtained on decomposing an aqueous polysulphide with mineral acid, is *soluble*—the yellow precipitate of sulphur formed in the spontaneous decomposition of free thiosulphuric acid is *insoluble*—in *bisulphide of carbon.*

Sulphur *boils* at 440°, and is converted into an intensely orange-yellow vapour of the density $S_8=96$ $(H=1)$. All varieties of sulphur are insoluble in water.

340. *Reactions of the substance Sulphur S_x:*

Nitrogen, Gold, Platinum are the only ordinary elementary substances upon which sulphur does *not* act at any temperature.

Oxygen.—Sulphur is readily inflammable in air or oxygen. It burns with a blue flame into gaseous dioxide SO_2 ('sulphurous acid'), which, in absence of *water*, does *not* act upon additional oxygen at any temperature.

Hydrogen.—If sulphur-vapour and this gas are heated together they undergo partial association into H_2S.

Chlorine.—See § 300.

Phosphorus, boron, silicon, each at certain temperatures, act on sulphur, and are converted into sulphides.

Carbon, when heated to redness in sulphur vapour, is converted into the bisulphide CS_2.

All ordinary metals (except Au and Pt) unite directly with sulphur, many with great avidity. A strip of copper or silver foil, for instance, when introduced into sulphur vapour, instantaneously becomes incandescent, and is burned into sulphide. Mercury also readily combines with sulphur at comparatively low temperatures. On the other hand, aluminium may be cited as an example of a metal which does *not act* on sulphur at any but very high temperatures. Sulphur can be distilled over aluminium without acting upon it.

Alkalies.—Sulphur readily fuses together with certain proportions of alkaline carbonates or hydrates. The fused mass (*hepar sulphuris*) is brown, and consists of sulphide or polysulphide, and sulphate, besides the excess that may have been used of reagent. Sulphur readily dissolves in boiling solutions of fixed caustic alkalies, also in such of baryta or strontia, and in milk of lime. The solutions contain *sulphide*, or polysulphide, and *thiosulphate*. Generally some sulphate is produced at the same time.

Liquid oxidizing agents.—When sulphur is heated in strong *nitric acid*, or in strong *hydrochloric acid* with gradual addition of *chlorate* of *potash*, it is gradually oxidized into, and dissolved as, sulphuric acid.

General Reactions of the Element.

341. Any sulphur compound, when kept at a red heat with excess of a mixture of *carbonate* (or *hydrate*) and *nitrate of fixed alkali*, is changed so, that the whole of the sulphur is ultimately obtained as *alkaline sulphate*, R_2SO_4. The nitrate in this reaction may be replaced by any of a certain class of oxidants, *e.g.* by alkaline chlorate or chromate. If, instead of such oxidizing agents, certain *reducing agents* (*e.g.* charcoal or carburetted hydrogens) are made to act conjointly with the *basic alkali*, the sulphur is, partly at least, converted into *alkaline sulphide* R_2S. Upon these facts are founded two general methods of sulphur-detection, which, with non-volatile solids, may assume the following forms:—

342. *Method of oxidation.*—Reduce the substance to a fine powder, mix it with 10-15 times its weight of *carbonate of soda*, and then incorporate with the mixture as much of *nitre* as will presumably suffice for a complete oxidation.* Now, first of all, make sure of the mixture not being *explosive*, by heating a very small portion of it on a piece of platinum foil and watching the effect. If the sample burns off with explosive violence, add to the rest enough of chloride or carbonate of sodium to moderate the reaction. Project the mixture, small quantities at a time, into a red-hot crucible, and ultimately maintain a red heat, until the oxidation is completed. The fused mass is exhausted with water, and, after filtration and supersaturation with hydrochloric acid, the sulphuric acid precipitated with *chloride of barium*, as $BaSO_4$. (See § 360.)

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* One part of *pure sulphur* requires about seven parts of nitre.

343. *Method of reduction.*—Mix a small quantity of the substance with carbonate of soda, and heat the mixture on charcoal in the reducing flame until the flux has crept into the charcoal. Now break out those parts of the latter which are impregnated with the flux, place them on a polished surface of silver (a silver coin for instance), and soak it in water. The sulphide dissolves and acts on the silver, with formation of a *black stain* of Ag_2S.

344. II.—*Sulphur acids.*

The following is a list of the hydrogen-salts and anhydrides of all known sulphur acids :—

	Formula of	
	Acid.	Anhydride.
(1.) *Monothionic acids.*		
Sulphhydric acid	*H_2S	...
Hydrosulphurous acid . .	H_2SO_2	SO
Sulphurous ,, . .	H_2SO_3	*SO^2
Sulphuric ,, . .	*H_2SO_4	*SO_3
(2.) *Dithionic acids.*		
Thiosulphuric acid . . .	$H_2S_2O_3$	S_2O_2
Hyposulphuric ,, . . .	*($H_2S_2O_6$)	S_2O_5
(3.) *Polythionic acids.*		
Trithionic acid	$H_2S_3O_6$	S_3O_5
Tetrathionic ,, ...	*($H_2S_4O_6$)	S_4O_5
Pentathionic ,, ...	*($H_2S_5O_6$)	S_5O_5

Note.—Of these formula, only those marked with asterisks * represent known chemical species ; those in brackets, however, are known only as aqueous solutions.

All these acids, with exception of hydrosulphurous, are decidedly *dibasic.*

345. Sulphhydric acid H_2S (sulphuretted hydrogen) is a colourless gas of 1·178 spec. grav. (air$=$1), endowed with an intense characteristic odour. (Rotten eggs smell of H_2S.) It is absorbed by water, and, more readily, by alcohol; by both the more largely the lower the temperature. One gramme of water, when shaken, at 15°, and under 760 mm. pressure, with excess of pure sulphuretted hydrogen, dissolves 4·91 mgr. of the gas = 3·23 cc. at 0° and 760 mm.* The dissolved gas is easily expelled by boiling, and displaced by absorptiometric exchange for any other gas; hence even dilute solutions exhibit a comparatively strong smell. If the solution is exposed to the air the dissolved gas is slowly oxidized with formation of a precipitate of sulphur. Sulphuretted hydrogen, when passed through a red-hot glass tube, undergoes dissociation into hydrogen and *sulphur*, which latter forms a deposit in the tube. When passed over red-hot *copper* (or any other of a large class of metals, of which, however, copper works best as a reagent for the purpose), it is readily reduced to hydrogen, with formation of metallic sulphide. The gas is readily inflammable; it burns with a blue flame into sulphurous acid and water. A porcelain plate held in the flame gets covered with a deposit of sulphur. If this experiment is tried with a flame of *hydrogen* contaminated with a trace of the sulphide, no sulphur can be collected, but the flame, where it strikes the porcelain, exhibits a characteristic *blue* colour. This is a most delicate test. The *reactions* of sulphhydric acid and of its solution may be supposed to be known to the student; suffice it to state that small quantities of the gas, when given as an admixture in another gas, *e.g.* air, are best detected by its smell, and by its tarnishing action on metallic silver or on a strip of paper moistened with a solution of *acetate of lead* or of *sulphate of copper*. Silver or mercury salts are not so well adapted for the purpose, because they are blackened also by other gases than H_2S; silver salts, for instance, by AsH_3, SbH_3, PH_3.

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* Hence 6·92 cc. contain H_2S=34 mgr. and suffice to precipitate Pb=207 mgr. of lead, etc. etc. No ordinary sulphuretted hydrogen water will ever quite come up to this standard.

Metallic sulphides may all be looked upon as salts of sulphuretted hydrogen, or as compounds of such salts with more sulphur; *i.e.* as being $n(H_2S)-mH+mR'+S_x$, where $m \leqq 2n$.

346. Sulphides of the metals of the potassium and barium groups can be formed (1.) by direct synthesis from the elements; (2.) by reducing the sulphates, at high temperatures, by means of hydrogen or carbon; (3.) by boiling the solutions of the hydrates in water with sulphur; (4.) by treating such solutions with sulphuretted hydrogen;—and in a variety of other ways. If operation (4.) is applied to aqueous caustic *potash*, *soda*, or *ammonia*, the hydrate in each case is next converted into R_2S, which, by an excess of the gas, is transformed into sulph-hydrate RHS. All these *sulphides* are soluble in water, the alkaline sulphides very readily. The colourless solutions are strongly alkaline to test-paper, and when mixed with any *decided acid* are readily decomposed, with elimination of *sulphuretted hydrogen*. Even carbonic acid decomposes them (partially) with formation of carbonate. If the solutions are exposed to the air, they slowly absorb oxygen, and assume a *yellow* colour, in consequence of the formation of di- or poly-sulphides (Ex. $2K_2S+O=K_2O+K_2S_2$). The solutions (of R_2S and RHS) dissolve sulphur, with formation of polysulphide $R_2S.S_x$ (where x is always < 4), and, in case of RHS, evolution of sulphuretted hydrogen. Such a polysulphide solution, when exposed to the air, gradually loses its colour in consequence of absorption of oxygen and conversion of the sulphide into thiosulphate, or thiosulphate and sulphur. The solutions of R_2S or RHS of potassium, sodium (and ammonium), readily dissolve precipitates of As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5; the sulphides K_2S and Na_2S dissolve also *mercuric sulphide;* alkaline polysulphides generally dissolve all the sulphides of the arsenic group, including those of gold, platinum, molybdenum, and tungsten. The solutions of all these thio-salts, when mixed with excess of hydrochloric acid, are completely decomposed, with precipitation of the acid sulphide and of the excess of sulphur that may be present, and evolution of *sulphuretted hydrogen*. The chief points of difference between the *alkaline* sulphides and the *barium-group* sulphides are, that the latter are less easily soluble in water (CaS is almost insoluble), and that their solutions possess less stability, being prone to decompose with formation of hydrates or oxysulphides.

Aqueous solutions of the class of sulphides and of the thio-salts just considered, are recognised by their strong alkaline reaction on litmus or turmeric, by their behaviour to acids, and by their readily attacking *metallic silver*, with formation of the black sulphide Ag_2S. Solutions of *alkaline sulphides*, when mixed with *nitroprusside of sodium*, assume a beautiful and very intense *purple* colour, which, however, does not come out in presence of caustic alkali. An aqueous solution of sulphuretted hydrogen does *not* exhibit this reaction.

347. **Sulphides of magnesium, aluminium, chromium**, can be produced in the dry way; but all these compounds, when treated with water, are decomposed with formation of hydrates and sulphuretted hydrogen.

348. **'Heavy-metallic' sulphides**; *i.e.* sulphides of the metals of the arsenic and copper groups, and of iron, nickel, cobalt, zinc, manganese. Each of these metals forms, in general, a series of sulphides, which, as a rule, besides those particular sulphides which correspond to the basic oxides of the metal, includes a number of lower and higher terms, of which the corresponding oxides, in many cases, are not known. Besides these simple sulphides, there is a great variety of complex ones, formed by the simultaneous union of sulphur with two or more heavy metals. The large classes of minerals known by the generic names of *pyrites*, *blendes*, *fahlores*, and many of the so-called *glances*,* are simple or complex heavy-metallic sulphides. Of the various

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* Some of these are arsenides.

methods by which heavy-metallic sulphides may be produced, the following are the most important:—(1.) Precipitation of solutions of haloids or oxygen salts of the metals by sulphuretted hydrogen or alkaline sulphides. (2.) Combustion of the metals in sulphur-vapour or exposure of a mixture of metal and sulphur to a high temperature. (3.) Ignition of the metals or metallic oxides in sulphuretted hydrogen. (4.) Reduction of the sulphates or of higher sulphides in hydrogen at high temperatures. (5.) Fusion of the metals or oxides with ready-made alkaline polysulphide or with a mixture of alkaline carbonate and sulphur. This operation results, in general, in the formation of alkaline thio-salts, of which, however, only those of the arsenic-group metals are soluble in water without decomposition. It is worth stating that even gold and platinum can be sulphurized in this manner. The precipitated sulphides are generally amorphous, and in some cases contain chemically combined water. Those resulting from dry-way operations and the native sulphides are anhydrous, and, as a rule, more or less distinctly crystalline and endowed with a metallic lustre.

349. *All heavy-metallic sulphides*, when heated in a draught-tube, give off *sulphurous acid*, and yield residues, or sublimates, of oxides, oxysulphides or—in case of silver, gold, platinum, mercury—of metals. When fused with *alkaline carbonate* or slightly hydrated *caustic alkali*, they generally give up part of their sulphur to the alkali, with formation of alkaline sulphide. This distinguishes them from the sulphates, which, under these circumstances, yield hepars only in *presence of reducing agents*. Heavy-metallic sulphides when kept at a red heat in *dry hydrogen*, behave differently: the compounds ZnS, MnS, FeS, Cu_2S (and substantially also Ni_2S), remain unchanged. Higher sulphides of the same metals are reduced to these particular sulphides. The sulphides of lead and cobalt leave residues of variable composition. The sulphides of (gold, platinum)* silver, bismuth, antimony, are reduced to metals, which remain as non-volatile or (in case of Sb) difficultly volatile reguli. The sulphides of cadmium and mercury are volatilized, the former slowly, the latter readily, with at least partial reduction to the metallic state. When exposed to a current of *dry chlorine* they are all readily and completely decomposed, some at the ordinary temperature, others on application of heat, with formation of metallic chlorides and chlorides of sulphur. (Comp. § 302.)

350. *Behaviour to mineral acids.*—The sulphides of antimony, tin, lead, bismuth, cadmium, manganese, zinc, iron, when given in a sufficiently fine state of division, can *generally* be decomposed by means of boiling strong (or even dilute) *hydrochloric acid*, with evolution of sulphuretted hydrogen and formation of solutions of chlorides. There are however some exceptions; thus, for instance, the iron-sulphide FeS_2 (pyrites) is not attacked by hydrochloric acid at all. The sulphides of the metals not included in the above list, are either not at all, or only very slowly, attacked by hydrochloric acid, and non-oxidizing acids generally. *Any of the sulphides* under consideration (with exception only of those of gold and platinum) are readily disintegrated by means of hot *concentrated nitric acid*, with formation of products which are the same as if the first effect of the acid consisted in the elimination of the sulphur as such, and in the conversion of the metals into oxides. Hence in the case of *antimony* or *tin*, the metal separates out as an insoluble oxide; *lead* is partially converted into (insoluble) sulphate, the rest into (soluble) nitrate; any of the rest of the metals are dissolved, mainly as nitrates. All these decompositions may be effected with an acid of 1·4 spec. gravity; but as the boiling point of such an acid lies above the melting point of sulphur, its action often stops short of a complete disintegration in consequence of some of the undecomposed sulphide being wrapped up in a coating of semi-fluid sulphur. This difficulty can be evaded by using strong fuming acid of 1·5 spec. gravity, which boils at 86°, *i.e.* far below the melting point of sulphur. By the combined action, in the heat, of strong *hydrochloric acid* and *chlorate of potash* (or by means of aqua regia), all heavy-metallic sulphides are decomposed and, in general, dissolved as chlorides.

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* These two can be reduced by the effect of heat alone.

351. Hydrosulphurous acid H-(SO)-OH.—It had been known for a long time that metallic zinc dissolves in cold aqueous *sulphurous acid* without gas evolution, but the true rationale of this reaction was only lately discovered by *Schützenberger*, who found it to consist in the formation of sulphite of zinc and free *hydrosulphurous acid*, according to the equation $2SO_2+Zn+H_2O=ZnSO_3+H_2SO_2$. The acid is known only as a constituent of this solution; of its salts the sodium compound $NaHSO_2$ only has been as yet obtained for itself. Both the hydrogen and the sodium salt are distinguished by the enormous avidity with which their solutions absorb atmospheric oxygen to pass into the corresponding sulphites. This must be borne in mind in carrying out the following process given by Schützenberger for the preparation of the *sodium salt*:—

Charge a flask with as much of granulated zinc as it will hold, then pour in enough of a concentrated solution of *bisulphite of soda* to cover the metal, close the flask with a good cork, and keep it in a cold water bath for about half-an-hour. A part of the zinc dissolves with formation of $NaHSO_2$, and of a double sulphite of zinc and sodium, of which latter salt a considerable portion crystallizes out. To remove the rest, run the liquid into three times its volume of strong alcohol, and allow to stand until the double sulphite has separated out as a precipitate, while the bulk of the hydrosulphite is still in solution. Then decant into bottles provided with good stoppers. The salt $NaHSO_2$ will gradually separate out in the form of a felt-like mass of thin colourless needles, which must be rapidly strained off and pressed between layers of bibulous paper. The salt may be purified by being dissolved in a little water, and reprecipitated with alcohol. It must be dried *in vacuo* or in an atmosphere of dry hydrogen. The *dry* salt Na-(SO)-OH is stable in air, but when moist or dissolved in water it rapidly absorbs oxygen with considerable evolution of heat. A solution of the *free acid*, or an acidified solution of the soda salt, when added to one of sulphate of copper, at once precipitates a mixture of copper and hydride of copper; from solutions of mercury or silver salts it precipitates the respective metals. It readily decolourizes *indigo* and *litmus* solutions by *deoxidation*, the bleached liquids regaining their colours on exposure to air.

352. Sulphurous acid.—The *anhydride* SO_2 is a colourless gas of 2·21 spec. grav. (air = 1), possessing a peculiar penetrating smell, and being condensible into a colourless liquid, which, under 760 mm. pressure, boils at $-10°$. The gas is largely absorbed by water. One gramme of water when shaken at 15° and 760° mm. (total) pressure, with excess of pure 'sulphurous acid,' dissolves 0·1353 grms. of the gas = 47·3 cc. at 0° and 760 mm.—(*Schönfeld.*) At $-6°$ a saturated solution deposits the crystalline hydrate $SO_2.9H_2O$.—(*Pierre.*) *Döpping*, under somewhat different circumstances, obtained crystals of the composition $SO_2.H_2O$. Both hydrates are very unstable. The aqueous solution, when subjected to the action of a current of any other gas, or when boiled, loses its dissolved gas. Towards test-papers and bases it behaves as if it contained the dibasic acid H_2SO_3.

353. Sulphites.—The normal and acid sulphites of the metals of the potassium group are easily soluble in water; of the rest of metallic sulphites, the normal ones are mostly sparingly soluble or insoluble in water, but, as a rule, more readily soluble, as acid salts, in aqueous sulphurous acid. The least soluble of all sulphites is the *lead salt* $PbSO_3$, which is less soluble in pure water than even the sulphate, but slightly soluble in aqueous sulphurous acid.—(*Gregory.*)

354. *Reactions of Aqueous Sulphurous Acid.*

The aqueous acid, when exposed to the air, always loses a part of the dissolved dioxide by absorptiometric exchange for air (hence its smell), but of the rest, a part undergoes gradual oxidation into *sulphuric acid.* The same transformation can be effected more readily and completely by means of certain oxidizing agents; thus, for instance: (1.) A solution of *iodine* in aqueous iodide of potassium, when dropped into one of sulphurous acid, is instantly decolourized. The reaction $H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI$, however, goes to the end only, if there is no less than about 3000 parts of water for every one of SO_2 present. (2.) *Chlorine* (*bromine*), even in concentrated solutions, readily converts sulphurous into sulphuric acid. (3.) A (purple) solution of *permanganate* of potash, when added to one of sulphurous acid, is decolourized, with formation of manganous and potassic sulphates. (4.) *Terchloride of gold*, by the action of sulphurous acid, is gradually reduced to metal. This reaction is accelerated by heating; the ones previously given go on readily enough in the cold. (5.) Hot *nitric acid* converts sulphurous into sulphuric acid.

355. *Aqueous Solutions of Sulphites*

when mixed with hydrochloric acid behave to the reagents named like such of the free acid in water. Tests (1.) and (2.) apply to neutral sulphites as well as to the acid, or rather better, inasmuch as the oxidations proceed more rapidly. In the case of *iodine* the oxidation is complete even in concentrated solutions, if there is enough of alkali present (as sulphite or carbonate) to saturate the whole of the acids formed in the process. *From neutral solutions of sulphites* (1.) *chloride* of *barium* precipitates the white sulphite $BaSO_3$, which is insoluble in water but readily soluble in dilute hydrochloric acid. If the solution is exposed to the air, it soon becomes turbid from *sulphate* of baryta; the same change can be effected instantaneously by means of any of the oxidizing agents named in § 354. (2.) *Nitrate of silver* gives a white crystalline precipitate, Ag_2SO_3, insoluble in water and somewhat slowly soluble in cold, but readily soluble in hot, dilute nitric acid.

356. *Sulphurous acid as oxidizing agent.*—A solution of a *sulphite* when added to an excess of *hydrochloric acid* which is being decomposed by *metallic zinc*, is reduced, with formation of sulphuretted hydrogen. (Comp. § 345). A mixed solution of *phosphorous* and sulphurous acids, when heated, deposits *sulphur*, with formation of phosphoric acid.

Sulphuric Acid.

357. **The anhydride** SO_3 forms white crystals of the appearance of asbestos. There are two modifications, one fusible at about 18°, and another which fuses only at about 100°. Either is readily volatilized at temperatures below 100°. The vapours, when brought in contact with moist air, form dense white clouds of hydrate. The anhydride is soluble in almost all proportions in the real acid; the solution when exposed to the air emits fumes of SO_3. '*Nordhausen sulphuric acid*' substantially consists of such a solution. Sulphuric anhydride acts most energetically on water, with formation of the real acid, or of higher hydrates, and evolution of much heat. At a red heat it breaks up into dioxide and oxygen, which, on cooling, do *not* re-combine.

358. *The real acid* H_2SO_4, exists, strictly speaking, only as a solid, which may be obtained in the form of crystals when liquid acid of exactly or nearly the composition H_2O+SO_3 is exposed to a temperature below 0°. Sometimes however the acid will not solidify even at the lowest temperatures. The crystals, when once formed, melt at 10°·3 into a colourless oily liquid of the spec. gravity 1·840 at 15° (water of $15° = 1$), which of course has the composition $H_2O.SO_3$, but cannot be assumed to consist altogether of H_2SO_4, as, on the application of the gentlest heat, it at once gives off fumes of SO_3. When boiled down in a retort, it behaves exactly *as if it was* a solution of SO_3 in a large excess of a stable hydrate $H_2SO_4+\frac{1}{12}H_2O$, boiling without change of composition (but with very considerable dissociation into SO_3 and H_2O) at 338°. The acid eagerly combines with water, with evolution of much heat and formation of a liquid mixture of higher hydrates. Of these, $H_2SO_4.H_2O$ can be obtained in crystals, which melt at 8°·5. According to *Pfaundler*, the quantities of heat evolved in the conversion of one gramme of liquid H_2SO_4 into liquid

$H_2SO_4.H_2O$	$H_2SO_4.2H_2O$	$H_2SO_4.3H_2O$	$H_2SO_4.120H_2O$
=69·7	103·4	118·9	181·2*

thermal units. Sulphuric acid, on account of its great avidity for water, is much used for the dehydration of such liquids or gases as are not affected by it chemically; but obviously, for gases at least, the hydrate $H_2SO_4.\frac{1}{12}H_2O$ is the proper preparation to use. Sulphuric acid readily dehydrates not only hydrates properly so called, but even many of those substances which contain water only potentially. The so-called *carbo-hydrates* (amylum, sugars, etc.), for instance, by the action of the acid, are decomposed, with formation of (*black*) *charcoal.* This property is exhibited even by an acid which contains somewhat more than $1H_2O$ for $1SO_3$.† More highly hydrated acid, when evaporated in a water-bath, ultimately attains the strength of $H_2SO_4.2H_2O$ (about); the residue when boiled down loses pure vapour of water until it has attained a certain strength which corresponds approximately to $H_2SO_4+H_2O$; on further concentration the vapours become more and more strongly acid, until at last they have the same composition $H_2SO_4.\frac{1}{12}H_2O$ as the residue.

Action on metals.—Of ordinary metals, *gold* and *platinum* are the only ones which are *not* attacked at any temperature by sulphuric acid of any concentration; all the rest, when treated with *concentrated* acid at the requisite temperatures, are converted into sulphates with evolution of sulphurous acid. *Dilute sulphuric acid*

Does *not* act on—		It converts into sulphates, with evolution of hydrogen—	
Au, Pt, Ag, Hg, Pb,	Cu, Bi, Sb,	Cd, Ni, Co,	Fe, Al, Mn, Zn, Mg,
even in presence of air.	in absence of air.	(slowly)	(readily).

359. Metallic sulphates.—Sulphuric acid, in opposition to the bases R'_2O and $R''O$, and wet-way reactions at least, is the strongest of known acids. With the bases R_2O of the *potassium* group, it is capable of forming three series of salts, viz. normal salts R_2SO_4, acid salts proper $RHSO_4$, and anhydro-sulphates $R_2SO_4.SO_3$. With the oxides of divalent metals it readily unites into normal sulphates $R''SO_4$, which are not capable of combining with H_2SO_4 or SO_3. Lithia and oxide of silver behave to sulphuric acid like oxides of divalent metals. The oxides R_2O_3 of iron, aluminium, etc., form a variety of sulphates besides the normal salts $R_2(SO_4)_3$. The normal sulphates of the metals of the potassium and barium groups and of lead are stable at even a bright red heat. The acid salts $R'HSO_4$ and $R'_2SO_4.SO_3$, at this temperature, lose their excess of acid. The sulphates $R''SO_4$ of zinc, magnesium, copper, cadmium, nickel, cobalt, and manganese, stand a *dull red heat* without decomposition; at considerably higher temperatures they are decomposed, with elimination of SO_3 or (SO_2+O) or both.

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* Maximum amount of heat obtainable. An acid of about the composition $H_2SO_4.3H_2O$ (spec. gr.=1·551, at 15°) may conveniently serve as a stock for preparing more largely diluted acids.

† Hereupon is founded an excellent method for the detection of free sulphuric acid in vinegar: Dissolve in the suspected vinegar a small quantity of cane-sugar, and evaporate as far as possible in a water bath. If H_2SO_4 was present, the residue is black.

The sulphates of the *sesquioxides* are readily decomposed by ignition into oxide and more or less largely dissociated vapour of acid. The ferrous salt, when exposed to a bright red heat, is reduced ultimately to the oxide Fe_2O_3, according to equations $2FeSO_4 = SO_2 + \{Fe_2O_3.SO_3 = Fe_2O_3 + SO_3\}$.

Metallic sulphates as a class, are crystalline salts, soluble in water. Of insoluble or sparingly soluble normal sulphates, the following are the most important: Sulphate of *baryta*, which is practically insoluble in water and dilute acids generally; the sulphates of *strontia* and *lead*, which are almost insoluble in water, but (the Sr-salt sparingly, the Pb-salt more readily) soluble in hydrochloric acid; the sulphates of *lime* $CaSO_4.2H_2O$, and of *mercurosum* Hg_2SO_4, which dissolve in about 500 parts of cold water (the lime salt is readily soluble in hydrochloric acid); sulphate of *silver* Ag_2SO_4, which requires 200 parts of cold water for solution. The normal sulphates of *bismuth* $(Bi_2O_3.3SO_3)$ and of *mercuricum* $(HgOSO_3)$ are decomposed *by water*, with formation of insoluble basic salts. There is a large number of insoluble *basic* sulphates of di- and poly-atomic metals, which however are mostly soluble in hydrochloric acid. Most sulphates are insoluble in absolute and very sparingly soluble, if at all, in ordinary *alcohol.* The hydric sulphates HRO_4 of potash and soda are decomposed by alcohol into normal salt and free acid.

360. *Reaction of Solutions of Sulphates.*

Chloride of barium gives a white powdery precipitate of sulphate of baryta, insoluble in water and in all ordinary salt solutions, and as good as insoluble in dilute acids (comp. § 216). The reaction, though in general very delicate, may fail in presence of a certain class of salts (including chloride of magnesium, nitrate of ammonia, and the metaphosphates of the alkalies) which, having the power of dissolving sulphate of baryta more or less largely, may prevent its separation. The precipitate has a great tendency to 'carry down' certain soluble salts, *e.g.* the nitrates of baryta and soda, by 'surface attraction,' and consequently when formed within a complex solution of salts is liable to be impure. Both these sources of error do not make themselves felt to anything like the same extent in the precipitation of barium by an *excess* of sulphuric acid.

This is the most delicate and characteristic test for sulphuric acid. The only substances which, in its application, might possibly be mistaken for sulphate of baryta, are the fluosilicate $BaSiF_6$, and the selenate $BaSeO_4$. Of these the former can be distinguished from the sulphate by its *not* yielding a 'hepar' when fused on charcoal with carbonate of soda in the reducing blowpipe-flame (comp. § 343). Regarding the discrimination of the selenate, see the chapter on *Selenium.*

361. **Hyposulphuric acid** $H_2S_2O_6$ (Syn. Dithionic acid).

A solution of the manganese salt of this acid is formed by the action, in the *cold*, of aqueous sulphurous acid on finely divided binoxide of manganese; thus, $MnO_2+2SO_2=MnS_2O_6$. A part of the SO_2—which however is the less the lower the temperature—is always oxidized into sulphate : $MnO_2+SO_2=MnSO_4$.

The *free acid* $H_2S_2O_6$ is known only as an aqueous solution, which, by evaporation at a gentle heat, or, what is better, by prolonged exposure to an atmosphere kept dry by means of oil of vitriol, can be brought up, undecomposed, to a specific gravity of 1·35 (about). On further concentration it gradually breaks up into sulphuric and sulphurous acids. More dilute solutions are decomposed similarly on boiling; but as long as there is a sufficiency of water present, a *complete* decomposition of the acid can probably not be effected by this operation. Of all di- and polythionic acids, in fact, hyposulphuric is the one which opposes the highest degree of stability to the influence of heat or chemical agents. In aqueous solutions (whether acid or alkaline) it is not acted on, in the cold, by *sulphuretted hydrogen*, *chlorine*, *bromine*, *iodine*, *permanganic acid*, or *chromic acid;* and, even when treated in the *heat* with *chlorine*, or *hydrochloric acid* and *chlorate of potash*, it is only *very slowly* oxidized into sulphuric acid. It is questionable whether the acid can be *completely* oxidized otherwise than by *fusion* of its salts with *nitre* and *alkaline carbonate* or equivalent oxidants. **Metallic hyposulphates.**—Hyposulphuric acid, although by theory dibasic, does not seem to be capable of forming acid salts $R'HS_2O_6$ with monovalent metals. The normal salts are *all soluble in water.* On ignition they are all decomposed according to the equation $R''S_2O_6 = SO_2 + R''SO_4$, where $R'' = K_2$, Na_2, Ba, etc. The sulphate, if stable at the temperature, remains as a residue.

Solutions of hyposulphates, as such, are *not* precipitated by any known reagent. When mixed with hydrochloric acid, they exhibit the reactions of the free acid. When boiled with mercury-, silver-, or lead-salts, they do *not*, like thiosulphates, yield precipitates of heavy-metallic sulphides.

361 *a.* Dilute solutions of hyposulphates, or sulphates, are *not* affected by the action of nascent hydrogen ($Zn + xHCl$) in *the cold.* In the heat, or from concentrated solutions generally, a part of the sulphur is eliminated as H_2S.

362. Thiosulphuric (formerly called '*hyposulphurous*') **acid.** — The anhydride S_2O_2 is not known. The acid $H_2S_2O_3$ *is* known, but only in the form of highly unstable aqueous solutions. When a cold dilute solution of a thiosulphate is mixed with hydrochloric or dilute sulphuric acid, the mixture remains clear for some time, but, on standing, the acid soon breaks up into sulphur, which separates out as a *yellow* precipitate (see § 339) and sulphurous acid. The decomposition sets in immediately on boiling. The hyposulphites $R'_2S_2O_3$ of the alkali-metals can be formed (1.) by the action of sulphur on solutions of the respective sulphites (Ex.: $Na_2SO_3 + S = Na_2S_2O_3$); (2.) by the action of sulphurous acid on solutions of the sulphides or polysulphides (Ex.: $2Na_2S + 3SO_2 = 2Na_2S_2O_3 + S$); (3.) by the action of atmospheric oxygen on the solutions of the polysulphides (Ex.: $Na_2S_5 + O_3 = Na_2S_2O_3 + S_3$), and in other ways.
All hyposulphites are decomposed when heated for themselves, with formation of sulphates and sulphides; some of them give off SO_2 or sulphur vapour, or both, at the same time (Ex.: $4K_2S_2O_3 = 3K_2SO_4 + K_2S_5$). Thiosulphuric acid, when given as an aqueous solution of the hydrogen, or of an alkaline or alkaline-earth salt, is readily oxidized into *sulphate* by the action of chlorine, bromine, permanganic acid, and other oxidizing agents. Neutral solutions, or solutions acidified with hydrochloric acid, of the thiosulphates of the metals of the potassium, barium, and magnesium groups, *readily decolourize iodine* solution, like sulphites, but the product of oxidation in all cases is a *tetrathionate* $S_4O_6R_2$, *not* a sulphate, as in case of a sulphite.

If a solution of a mercury-, silver-, or lead-salt is added to a neutral thiosulphate-solution, the thiosulphates of these metals are at first formed and precipitated; but the precipitates very soon, and on boiling immediately, suffer decomposition, with formation of the respective sulphides, which are easily recognised by their black colour (Ex.: $Ag_2S_2O_3 + xH_2O = Ag_2S + SO_3.xH_2O$). *Alkaline thiosulphates* have the power of dissolving ***haloid of silver***, with formation of soluble double salts (Ex. $AgCl + Na_2S_2O_3.H_2O = NaCl + AgNaS_2O_3.H_2O$). From such solutions the silver *cannot* be precipitated by means of alkaline chlorides, but it can be precipitated completely (as Ag_2S) by means of *sulphide* of *ammonium*, and also by boiling the solution with a large excess of *hydrochloric acid*, until all the thiosulphuric acid is decomposed, when the silver is obtained, ultimately, as a mixed precipitate of haloid and sulphide.

363. *Polythionic Acids.*

$H_2S_3O_6$, $H_2S_4O_6$, $H_2S_5O_6$.

Trithionic acid.—This acid is known only in the form of the potash salt $K_2S_3O_6$, which can be obtained : (1.) By digesting a solution of the acid sulphite with sulphur, $6KHSO_3 + S_2 = 2K_2S_3O_6 + K_2S_2O_3 + 3H_2O$. (2.) By treating a concentrated solution, in 8°/o alcohol, of the neutral thiosulphate with sulphurous acid, $2K_2S_2O_3 + 3SO_2 = 2K_2S_3O_6 + S$. (3.) By the action of the acid sulphite on the neutral thiosulphate. A mixed solution of the two salts, when allowed to evaporate, deposits crystals of trithionate, which, however, seems to be formed only at the moment of crystallization, $6KHSO_3 + K_2S_2O_3 = 2K_2S_3O_6 + 2K_2SO_3 + 3H_2O$ (?)

Tetrathionates are formed by the action of iodine on solutions of the thiosulphates of K, Na, Ba, H, etc. (Ex.: $2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$).

Pentathionic acid $H_2S_5O_6$ is formed by the action upon one another of water, sulphurous acid, and sulphuretted hydrogen : $xAq + \{5H_2S + 5SO_2 = H_2S_5O_6 + 5S + 4H_2O.\}$

364. *Polythionates*, as a class, are highly unstable compounds. The hydrogen salts are known only as aqueous solutions, which, when concentrated by evaporation in the heat, break up (trithionic acid almost immediately, the other two after having passed certain degrees of concentration), with precipitation of *sulphur*, and formation of *sulphuric* and *sulphurous* acids. Their silver and mercury salts, as produced ephemerally by addition of solutions of salts of these metals to solutions of alkaline polythionates, are readily decomposed, especially on heating, with formation of precipitates of sulphides. Hence it appears that the polythionic acids, while widely differing from sulphuric, sulphurous, and hyposulphuric, are not unlike the thiosulphuric acid, from which, however, they differ by the great instability of their alkaline salts. Polythionates, like sulphites and thiosulphates, are readily *oxidized* in *acid*, and more easily still in alkaline solutions, by means of *chlorine*, *bromine*, or *permanganate of potash*, with conversion of the whole of their sulphur * into *sulphate*. These oxidations go on in the cold, which distinguishes the acids from hyposulphuric acid, which by these agents is attacked only in the heat.

The following table—which supposes the several acids to be given as solutions of their potash or soda salts—affords data for the discrimination of the polythionic acids and of thiosulphuric acid. Given solutions of, respectively—

$R_2S_2O_3$	$R_2S_3O_6$	$R_2S_4O_6$	$R_2S_5O_6$
—Then (1.) these solutions when mixed with **hydrochloric acid** are decomposed with elimination of $H_2S_xO_y$, which when concentrated by evaporation in the heat, breaks up—			
At once,		As soon as a certain degree of concentration is passed,	
with formation of *sulphur*, *sulphurous acid*, and			
Nothing else.	$\longleftarrow$ *Sulphuric acid.* $\longrightarrow$		
(2.) If the solutions are mixed with excess of **caustic potash** and boiled, then			
$R_2S_2O_3$ remains unchanged.	The polythionates break up, with formation of *thiosulphate* as a constant product, and of, respectively,		
	R_2SO_3 and R_2SO_4.	R_2SO_3 and R_2S.	R_2SO_4 and R_2S.
(3.) † If the solutions are boiled with excess of **mercuric cyanide** the salts suffer complete decomposition, with formation, pro molecule $R_2S_xO_y$, of $1HgS+2HNC+$, respectively—			
H_2SO_4.	$2H_2SO_4$.	$2H_2SO_4+S$.	$2H_2SO_4+S_2$.
(4.) **Mercurous nitrate** produces			
An *immediate* black precipitate of HgS.		A yellowish precipitate which blackens only on boiling.	

From these statements it is easily seen how any *one* of the four acids can be identified, with more or less certainty. The analysis of a mixture of two or more of them can in general only be effected indirectly, by quantitatively determining the relative amounts of sulphur, oxygen, and metal present in the mixture. [Compare (3.) in table.]

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* Except perhaps part of that which, in case of $H_2S_2O_3$ or $H_2S_5O_6$, may separate out as sulphur in the process.

† These reactions were discovered and studied by *Kessler*, who recommends them for determining the composition of the several acids. In case of thiosulphates, nitric acid must be added (after the $HgCy_2$) in successive small portions, and, after each such addition, the mixture boiled, until the precipitate, which is at first yellow, has become black.

365. *Summary of Properties and Reactions of Thionates.**

1. **Characteristic smells exhibited** by: sulphuretted hydrogen and by sulphurous acid.

2. **Metallic silver stained**: by solutions of alkaline and alkaline-earth sulphides and by H_2S.

3. **Lead-paper discoloured**: by H_2S-gas.

4. **Solid thionates when heated in a sublimation-tube**: may give out water. Normal *sulphates* $R''SO_4$, if $R = K$, Na, $\frac{1}{2}$(Ba, Sr, Ca, Mg, Zn, Cu, Cd) undergo no other visible change. Other sulphates: decomposed in various ways.

Thionates, not sulphates, are, in general, decomposed. Those in which $R = K$, Na, $\frac{1}{2}$(Ba, Sr, Ca) behave as follows: *Sulphides* R_2S, no substantial change. Polysulphides $R_2S.S_x$ give off sulphur. *Sulphites* leave residue of R_2S and R_2SO_4. *Hyposulphates* break up into $SO_2 + R_2SO_4$. *Thiosulphates* and *polythionates* are decomposed in various ways; constant products: S, SO_2, and R_2SO_4.

5. **Small specimens when roasted in a draught-tube** behave as follows: *Sulphur* burns away as SO_2; polysulphides generally, and almost *all heavy-metalled sulphides*, behave as if part at least of the sulphur was free; residues from sulphides of alkali or alkaline-earth metals contain R_2SO_4; heavy-metallic sulphides leave oxides, or oxysulphides or metals.

Neutral or Alkaline Solutions of Thionates and Reagents.

6. **Excess of hydrochloric acid** liberates part, at least, of the acid, which, if it does not happen to be *sulphuric*, undergoes *some* change, sooner or later, when the mixture is boiled down. Supposing this operation to be performed upon the several individual thionates, then the phenomena described in the left column of the following table correspond to the thionates named in the other.

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* A generic term meant to include sulphur-acids, their metallic salts and their anhydrides.

a. H_2S given off freely.	(*a.*) Sulphides R_2S.
b. H_2S given off freely and sulphur or metallic sulphide precipitated.	(*b.*) Polysulphides R_2S or alkaline thio-salts.
c. Ready evolution of SO_2; ultimate residue clear and free from SO_4H_2.	(*c.*) Sulphites.
d. Very slow decomposition, with formation of SO_2 and R_2SO_4, which becomes marked only after considerable concentration.	(*d.*) Hyposulphates.
e. Mixture *readily* deposits yellow sulphur, with evolution of SO_2.	(*e.*) Thiosulphates, Trithionates.
α. Residue free of R_2SO_4.	(α.) Thiosulphates.
f. Mixture, if originally dilute, remains clear for some time, but, after sufficient concentration, yields S, SO_2 and R_2SO_4.	(*f.*) Tetrathionates, pentathionates.

7. **Chloride of barium** precipitates *sulphates*, *sulphites*, and, in concentrated solutions, also *thiosulphates.* $BaSO_3$ and BaS_2O_3 are soluble, $BaSO_4$ is insoluble in HCl. (No other thionates give precipitates with the reagent.)

8. **Nitrate of Silver,** when added to solutions of *thiosulphates* or *polythionates*, produces precipitates of the respective silver-salts, which, when allowed to stand in the cold, are more or less readily, and on boiling are all quickly, decomposed with formation of (black) *sulphide of silver.* In solution of *sulphates* or *hyposulphates* the reagent produces no change even on boiling. From *sulphites* it precipitates white Ag_2SO_3, which, although on boiling it may get discoloured by reduction to *metal*, is never thereby converted into sulphide.

9. **Iodine-solution** is not changed by sulphates, hyposulphates, tetrathionates, but when added to neutral, or dilute acid, solutions of *sulphites* or *thiosulphates*, it is readily decolourized, with formation of *sulphate* or *tetrathionate* respectively. (Comp. 7.)

10. **Chlorine, bromine, permanganic acid,** if applied in the *cold* to acid or alkaline solutions of *hyposulphates*, produce *no change* in the nature of the acid; all other *lower thionates*, when operated upon in this way, are oxidized into *sulphates*.

366. *Examination of an Aqueous Solution of Metallic or Hydrogen Salts for Thionates.*

The summary of reactions given in the preceding paragraph affords more than sufficient data for the identification of any *one individual* thionic acid, supposing it to be given in the form of a simple salt; but no combination of known reactions will enable one to frame even a theoretically valid method for the exhaustive analysis of any *mixture* of *thionates*, quite apart from any difficulties that might arise through the presence of foreign substances. We shall therefore at once substitute a part of the problem for the whole, and show how, in certain cases, this minor problem can be solved. What we mean to do is to show how a solution of *alkaline salts*—which, to be able to assume the simultaneous presence of any two or more of the acids under consideration, we must suppose to be alkaline to test-paper—can be examined for: A. Sulphates; B. Sulphides; C. Hyposulphates; D. Thionates, not A, B, or C, as a class; E. Thiosulphates and trithionates as a class; F. Sulphites and thiosulphates as a class.

367. To consider first a comparatively easy case, let us suppose the solution to be such that, when strongly acidified with *hydrochloric acid*, it remained clear even when exposed for a short time to a boiling heat. Such a solution could not possibly contain sulphides *and* sulphites, or the group E. To test for A and B, acidify a portion of the solution with hydrochloric acid in the cold, and search for H_2S (by means of *acetate-of-lead* paper, if necessary) and for H_2SO_4 by means of *chloride of barium*. If the salts R_2S are found absent, test for *sulphites* with *iodine solution*, and another portion for

D by seeing if the acidified liquid decolourizes *permanganate* in the cold. In both cases a negative result can be accepted as final, but a positive one requires to be confirmed, which, in reference to group D, can be done by means of *nascent hydrogen*, which, when applied to dilute solutions in the cold, does not affect sulphuric nor hyposulphuric acid, but eliminates H_2S from all other thionic acids. The safest method, however, is, after having completely eliminated the sulphuric acid by means of chloride of barium and free hydrochloric acid *in the cold and in absence of air*, to treat the filtrate with excess of *permanganate* and excess of *alkaline hydrate* in the cold, and after having dissolved the manganese oxides by means of hydrochloric acid and *ferrous chloride in the cold*, to see if an additional quantity of sulphate of baryta has been produced by this operation. The sulphur in this precipitate must have been present originally in the form of acids of group D. If the filtrate from the second $BaSO_4$ precipitate still contains sulphur (not SO_4R_2),—which, after supersaturation with pure alkaline carbonate and evaporation to dryness, can be searched for by means of one or the other of the two general tests for sulphur given in §§ 342 and 343—such sulphur must have been present originally as *hyposulphate*. This method for detecting *hyposulphuric acid* can obviously be applied directly to any mixture of thionates, including sulphides.* In absence of group D and of R_2S it assumes a very simple form ; all that is required in this case is first to remove the sulphuric acid, if present, by means of chloride of barium, and then to test the filtrate for sulphur, by one or the other of the two fundamental methods referred to.

368. If the solution is *alkaline*, it may contain any combination of thionates. But in any case, the salts R_2S, if present, are readily detected by means of metallic silver, and can be eliminated, and their sulphur separated, from the

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*** It must, however, be stated that, although theoretically correct, it has not yet been tested by direct experiments.**

rest by means of *acetate of zinc*, which precipitant must be added until a drop of the mixture, when applied to a silver coin, no longer produces a black stain. Supposing this to have been done, and the precipitate to have been removed by filtration and been properly washed, we have to deal with a *precipitate* containing, potentially, free sulphur, the sulphides of zinc and of the metals of the arsenic group, and perhaps also those of copper, mercury, and nickel; and a *filtrate*, which may contain *any thionates*, *not sulphides*. Before attempting any separation, it is expedient, first, by means of preliminary tests applied to separate portions, to try and form at least a notion of the potential complexity of the solution. What was said above, and Nos. 6-10 of the summary in § 365, will suggest methods for the purpose. Supposing all the reagents applied to have given positive answers, a partial analysis might be attempted as follows :—
Add excess of *chloride of barium* in the cold, allow to settle in a close vessel, and separate precipitate and liquid.

<table>
<tr><th>*The precipitate* may contain :</th><th colspan="3">*The filtrate* may contain :</th></tr>
<tr><td rowspan="3">**$BaSO_4$** : insoluble in hydrochloric acid.
$BaSO_3$: soluble in hydrochloric acid ; the solution decolourizes *bromine*-water and *iodine-solution*, with formation of a *precipitate* of $BaSO_4$.
BaS_2O_3 : soluble in hydrochloric acid ; the solution decolourizes *iodine*-solution, with formation of a *solution* of $R_2S_4O_6$; when heated it deposits yellow sulphur.</td><td>$R_2S_2O_3$ decolourizes iodine.</td><td>$R_2S_{3,4,5}O_6$</td><td rowspan="2">$R_2S_2O_6$ characterized by negative properties.</td></tr>
<tr><td colspan="2">Convertible into *sulphate* by alkaline *permanganate* in the cold.</td></tr>
<tr><td colspan="3">For further information, *vide* supra.</td></tr>
</table>

369.—III. *Organic Sulphur Compounds*

for the purposes of the Analyst may be classified as follows :—

1. **Thionates** of organic bases proper (*i.e.* bases such as quinine, ethyl-amine, etc. etc.)—Regarding these nothing need be said, except that, to conveniently identify them as salts of the respective acids, it is sometimes necessary to eliminate the base and replace it by potash or soda, which, as a rule, can easily be effected by means of the aqueous reagents bearing these names, or even by the corresponding carbonates.

2. *The large class of substances* **(CxHyOz).xSO**$_3$ producible by the

direct action of carburetted hydrogens, alcohols, acids, etc., on oil of vitriol, or sulphuric anhydride.—These may be divided into two classes:

(*a.*) **True sulphates** (Ex. Sulphate of ethyl $EO\text{-}(SO_2)\text{-}OE$*, ethylsulphuric acid $HO\text{-}(SO_2)\text{-}OE$, etc. etc.)—These substances when boiled with water—and their metallic salts when boiled with dilute hydrochloric acid—are more or less readily decomposed into the respective alcohols and *sulphuric acid.*

(*b.*) **Sulpho-acids proper,** *i.e.* such sulphuric acid derivatives in which the *sulphur* in the sulphuric-acid rest HSO_3 is combined *directly* with carbon. (Ex. Isethionic acid $HO\text{-}(C_2H_4)\text{-}SO_3H$; benzenesulphonic $(C_6H_5)\text{-}SO_3H$, etc.)—These acids are very stable compounds; they *cannot* be decomposed by boiling with *water*, and their sulphur cannot, as a rule, be eliminated completely as H_2SO_4 by even prolonged treatment with nitric acid in the heat. Their alkaline salts, when subjected to *dry distillation* with *caustic potash*, as a rule (which however has not yet been proved to hold with all known members of the genus) exchange their (SO_3R)'s for (OH)'s; thus for instance: $C_6H_5.SO_3K + KHO = C_6H_5.OH + SO_3K_2$ (phenol and alkaline sulphite). A great number of substances which, according to their mode of formation should be *acid sulphurous ethers*, are in reality members of the class of acids under consideration.

3. **Sulphides,** *i.e.* (*a.*) thio-ethers; (*b.*) thio-alcohols; (*c.*) thio-acids. [Ex. (*a.*) Sulphide of ethyl E_2S; (*b.*) mercaptan EHS; (*c.*) thiacetic acid $(CH_3)CO.SH$.]—This is a very well defined chemical genus; but there is no general reaction known by means of which its members might be readily identified *as sulphides*; there is, for instance, no general method of double decomposition for, say, replacing the sulphur by oxygen and eliminating it as H_2S or metallic sulphide. These sulphides, when boiled with nitric acid, are oxidized into sulpho-acids. In this process a part of the sulphur *may* be eliminated as sulphuric acid, but we cannot hereupon found a general method for its detection.

4. Other organic sulphur compounds.—This class, as is hardly necessary to say, includes a large number of chemical genera, each of them characterized by certain sets of reactions; but these reactions are, in general, not translatable into analytical methods.

The mere examination of an organic substance for *combined sulphur* can always be effected by means of the *general method of oxidation* given in § 342, which, however, when applied to such bodies which do not contain their sulphur in a *fixed* form, must be executed so as to force the vapours into contact with the red-hot reagents. A more convenient method, in such cases, is

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* $E=(C_2H_5)'$.

370. '*Carius*,' which is founded upon the fact that all organic sulphur compounds when heated in sealed-up glass tubes with nitric acid of 1·2 to 1·4 spec. gravity, to 120°-150° for a sufficient time, are either completely burned (into CO_2, H_2O, SO_4H_2, etc.), or at least changed so that all that ultimately remains unburned are sulpho-acids, which by super-saturation of the whole product (nitric acid, etc.), with alkali, evaporation to dryness and fusion of the residual alkaline salts in a silver dish, are easily destroyed, with conversion of their sulphur into alkaline *sulphate*. The strength of acid to be used, the temperature at which, and the time during which, it must be made to act, depend on the nature of the substance one has to deal with. Obviously the method applies also to all *inorganic* sulphur compounds, disintegrable by nitric acid.

371. *Examination of Solutions of Thionates for Metals.*

Solutions, in water or dilute mineral acids, of *sulphates* or *hyposulphates*, are accessible to the methods of metal-detection given in Div. II. *Sulphites*, on account of the decomposing action of free sulphurous acid on sulphuretted hydrogen, must, previous to the application of *this reagent*, be boiled with a convenient acid, *e.g.* hydrochloric, until all the SO_2 is expelled. Solutions of *thiosulphates* and *polythionates* exhibit anomalous metal-reactions, and must, consequently, preparatory to an exhaustive examination for their metallic constituents, be decomposed so as to bring the metals into more convenient states of combination. This can be done (1.) by treating the solutions with *excess of chlorine*, which, in general, produces a *precipitate*, consisting potentially of sulphur, chloride of silver, and sulphates of lead and of barium-group metals, and a solution of sulphates. The same process applies also to solutions of alkaline thio-salts, such as sulpharseniates, etc.; (2.) by boiling the solution, after sufficient concentration, with excess of *nitric acid*, until all that part of the sulphur which has not separated out as such is converted into *sulphate*. The result is the same as in method (1.)

372. *Disintegration of Insoluble Metallic Thionates.*

A mixture of *sulphides* insoluble in water can always be completely disintegrated by successive treatment in the heat with (1.) hydrochloric acid, (2.) nitro-hydrochloric acid, or hydrochloric acid and chlorate of potash. Native sulphides must, previous to the application of the liquid reagents, be reduced to a fine powder. (Consult §§ 349, 350, 302.)

Of the large class of insoluble *basic sulphates*, the vast majority can be decomposed and dissolved by means of hydrochloric acid.

All non-volatile insoluble sulphates, for instance the sulphates $R''SO_4$ of *baryta*, *strontia*, *lime*, *oxide of lead*, are readily decomposed by fusion with excess of alkaline carbonate. The fused mass, when treated with water, yields a precipitate of metallic carbonate and a solution of alkaline sulphate.

373. *Selenium and Tellurium.*

Two rare elements, which, in the atomic constitution of their compounds, are closely analogous to *sulphur*, while, in their general chemical character, they may be said to be intermediate between that element and arsenic. The following is a short summary of what, in their chemical history, is of most importance to the Analyst :—

Selenium, Se.	*Tellurium*, Te,
Elementary selenium and certain heavy metallic selenides occur in nature as rare minerals. Traces of the element are frequently found to accompany sulphur in native compounds, *e.g.*, in volcanic sulphur, in certain pyrites, etc.	is of rarer occurrence and less widely diffused than selenium. It occurs native as elementary tellurium, and in the form of heavy metallic tellurides. It is often found associated with sulphur, but rarely with selenium.

374. *The 'Free' Elements.*

Elementary Selenium

exists in a variety of allotropic modifications, which all melt at temperatures below 250°, and at a certain higher temperature (which lies below 860°) boil with formation of the same deep yellow vapour. Solid *amorphous* selenium is brittle, and presents a conchoidal fracture ; when seen in compact masses it appears very deep brown (almost black), but if spread out in thin layers it transmits red light. Spec. gr. = 4·3. It does not conduct electricity. At ordinary temperatures it is stable, but, when heated to 125°-180°, it gives out much heat and passes into the 'granular-crystalline' variety which has a bluish-grey colour and metallic lustre.

Elementary Tellurium

is a white crystalline brittle *metal* of about 6·2 spec. grav., which conducts electricity. At about 500° it melts, and at a certain temperature lying between 1040° and 1400° it boils, with formation of a greenish yellow vapour.

Both elements are insoluble in water; *one* of the crystalline varieties of selenium dissolves *sparingly* in *bisulphide of carbon.* Selenium is less inflammable, and tellurium *far* less so, than sulphur ; but either, when heated in air, is readily converted into *dioxide* YO_2.*

375. *Selenious* oxide SeO_2 is a white solid, which is infusible but readily sublimable below redness. It readily dissolves in water, forming a solution of

376. *Selenious acid* H_2SeO_3, which can be obtained in crystals. This hydrate is a powerful dibasic acid, being capable of decomposing even chlorides and nitrates in the heat.† [It is *not* volatilized from its aqueous solution on boiling.

Tellurous oxide TeO_2 is a white solid which, when heated, first *melts* into a yellow liquid, and then sublimes. The fused oxide on cooling solidifies into a crystalline mass.

Tellurous acid H_2TeO_3 cannot be produced synthetically, but is obtained, as a bulky white precipitate, by decomposing the tetrachloride by water. H_2TeO_3 is a comparatively weak dibasic acid. Both the oxide and its

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* Y = Se, Te.

† [ ] holds for the corresponding tellurium compounds, except that certain alkaline anhydrotellurites ($R_2O + 2$ or more TeO_2) are only sparingly soluble in water.

Its alkaline salts are soluble in water; most other metallic selenites are sparingly soluble or insoluble in water, but dissolve in hydrochloric acid.]	hydrate readily dissolve in hydrochloric and in nitric acid. The solutions, if not too strongly acid, are precipitated when diluted with water. The nitric solution when heated to 40° deposits crystalline *anhydride* TeO_2.

377. *Behaviour of Acid Solutions of ——ites* to Reagents.*

<table>
<tr><th>(The solutions are colourless.)</th><th>(The solutions are yellow.)</th></tr>
<tr><td colspan="2"><i>Sulphuretted Hydrogen,</i></td></tr>
<tr><td>precipitates a <i>yellow</i> sulphide SeS_2, which almost immediately breaks up into its elements. $(Se+S_2)$ is readily soluble in sulphide of ammonium.</td><td>precipitates the <i>brown stable</i> sulphide TeS_2, which is readily soluble in sulphide of ammonium.</td></tr>
<tr><td colspan="2"><i>Ammonia, or Carbonate of Potash</i>
(In absence of insoluble bases),</td></tr>
<tr><td>produces no visible change.</td><td>gives a white precipitate of TeO_2, soluble in excess of either reagent.</td></tr>
<tr><td colspan="2"><i>Sulphurous Acid</i></td></tr>
<tr><td>readily precipitates, at a gentle heat, free selenium, which is at first red, but, on standing, becomes greyish-black. The precipitate is soluble in cyanide of potassium solution.</td><td>(on boiling) precipitates <i>black</i> metallic <i>tellurium.</i> The precipitate is <i>in</i>soluble in aqueous cyanide of potassium.</td></tr>
<tr><td colspan="2"><i>Zinc, Stannous Chloride, and certain other reducing agents,</i>
act substantially like sulphurous acid; ferrous sulphate, however, produces no change.</td></tr>
<tr><td colspan="2"><i>Free Chlorine, also Chromic Acid,</i></td></tr>
<tr><td>when added in the <i>cold</i>, converts the selenious acid more or less completely into selenic acid.</td><td>No action?</td></tr>
</table>

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* *i.e.*, the compounds R'_2YO_3, where $R'=H$ or 1 equivalent of metal. What is given under 'selenium' holds also for the purely aqueous solution of the acid.

† It is very readily soluble also in a warm solution of neutral sulphite of potash or soda, with formation of seleno-sulphates. From the solutions the selenium can be precipitated (as Se) by hydrochloric acid.

378. *Selenates and Tellurates*

are produced when the free elements or their dioxides, or their compounds with metals, or any ——ites, are *fused* with *carbonate* and *nitrate of potash.* The fused mass contains alkaline ———ate R_2OYO_3, which is soluble in water. If the solution is acidified with *nitric acid*, and mixed with excess of *chloride of barium*, then

The *selenic acid* is precipitated as $BaSeO_4$, which is similar in appearance and in its behaviour to cold dilute *nitric acid*, to the sulphate.	The *telluric acid* remains dissolved. From neutral solutions a part of the acid may go down as $BaTeO_4.3HO$.
The *hydrate* $H_2SeO_4.H\ O$ is an oily liquid of 2·6 spec. gravity, which in its behaviour to water resembles oil of vitriol. When heated beyond 285° it breaks up into SeO_2, O, and H_2O. Selenic acid is a strong dibasic acid, similar in its chemical character to sulphuric.	The hydrate $H_2TeO_4.2H_2O$ forms colourless prisms, which are considerably, though slowly, soluble in cold and readily soluble in hot water. The solution reddens litmus but slightly. The hydrate loses its $2H_2O$ at 100°, and the residue when exposed to a certain temperature below redness is reduced to the anhydride TeO_3, an *orange-yellow mass*, insoluble in even hot water. When strongly heated, the trioxide breaks up into dioxide and oxygen.
Aqueous selenic acid *cannot* be reduced at all by zinc, iron, sulphuretted hydrogen, or sulphurous acid.	By the action of the reducing agents named under *selenic acid*, aqueous telluric acid is reduced —more or less slowly—to tellurous.

379. *Selenates and tellurates* generally, including the anhydrides (and not excepting even **selenate of baryta**), when boiled with *hydrochloric acid*, are completely decomposed, with formation of free chlorine and of solutions of the ——ous acids YO_3H_2. These same acids (not the acids YO_4H_2) are produced in the oxidation of the elements or of their metallic compounds by means of nitric acid or other aqueous oxidants, *even in* absence of chlorides.

380. Blowpipe Tests.

(1.) *When heated on Charcoal in the Reducing Flame.*

Most *selenites* and *selenates* give up a part of their selenium as free selenium, which in passing through the flame imparts to it an azure blue hue.	*Tellurium oxides* are readily reduced to metal which is volatilized, and in passing through the flame burns into a *white smoke* of dioxide. A part of the oxide is deposited on the charcoal. The deposit, when touched with the reducing flame, is volatilized, with production of *green* light.

(2.) *When heated with Carbonate of Soda on Charcoal in the Reducing Flame.*

Non-volatile *selenium* compounds yield a flux (containing alkaline *selenide*), which, when moistened with water on a silver coin, produces a dark brown stain.	Non-volatile *tellurium* compounds are, at least partially, reduced with formation of a smoke and deposit of *dioxide.* (*Vide supra.*) Part of the metal remains in the flux as *telluride.*

(3.) *When fused together with Borax.*

Selenium oxides exhibit no characteristic phenomena. *Note.*—It is a highly characteristic property of selenium vapours that their *oxidation in a flame* always creates an *intense nauseous smell,* not unlike that of putrid horse-radish. This often enables one to detect the least traces of selenium in presence of tellurium or other elements.	*Tellurium oxides,* in the oxidizing flame, yield *colourless* beads, which, when heated in the reducing flame on charcoal, become *opaque and grey* from reduced metal.

III. NITROGEN.

381.—I. *Free Nitrogen* N_2

is a colourless permanent gas of 0·9714 spec. grav., (air=1). Its 'coefficient of absorption' by water, at 15°, is=0·0148; *i.e.* one volume of water when shaken with excess of nitrogen of 760 mm. partial pressure at 15°, absorbs a quantity of N_2 gas, which, if measured by itself at 0° and 760 mm., would amount to 0·0148 volumes. Pure atmospheric air, when freed from the small quantities of carbonic acid and vapour of water which it invariably contains, is a mixture in almost absolutely constant proportions of nitrogen and oxygen; the former gas forming 76·8 °/₀ by weight, or 79·0 °/₀ by volume, of the whole. Chemically, nitrogen is characterized mainly by *negative* properties. There are, it is true, a few reactions in which it is known to take part: it combines, at a red heat, with *titanium*, *tungsten*, *magnesium*, and perhaps one or two other (of the rarer) elements; when passed over a white-hot mixture of *charcoal* and caustic *alkali* or *baryta*, it is absorbed as *cyanide;* a mixture of *nitrogen* and *oxygen* when *locally* heated by means of electric sparks, yields traces of nitrogen-oxides;—but none of these reactions are practically available for the identification of the *chemical species* N_2.

(382.)—II. *Ammonia* NH_3.

Regarding this substance and the salts producible by its union with real acids, see §§ 260-270.

Of other inorganic *ammonia-derivatives*, the following may be named: (1.) The compounds formed by the direct union of anhydrous ammonia with *acid-anhydrides.* (Ex. $SO_3 + 2NH_3 = H_2N\text{-}(SO_2)\text{-}O\text{-}NH_4$; sulphamate of ammonium.) All these compounds, when treated with water, are either at once converted into, or at least behave to aqueous *caustic alkalies* in the heat as if they were, ammonium salts of the original acids. (2.) The large class of compounds producible by *the union of* ammonia with certain *metallic haloids* and other classes of *metallic salts*. In most of these substances the NH_3 is so loosely combined with the rest, that it is easily separated by the application of comparatively low degrees of heat or by the action of water. This is the case, for instance, with the compounds of ammonia with the chlorides of *silver* and *calcium*. In others however, as for instance in the salts of the so-called *platinum bases*, the NH_3 is in firm *atomic* combination with the rest, so that it can, in general, be regenerated only by prolonged treatment of the substances with strong aqueous potash in the heat. (3.) The *metal-amides* and the *nitrides:* compounds of metallic or semi-metallic elements with the ammonia-residues $(NH_2)'$ or $(N)'''$. The following is a list of the most important of these substances: KNH_2; $Zn(NH_2)_2$; K_3N; Mg_3N_2; Fe_4N; CrN; VN, VN_2; BN; $SiNx$. They are all solids, and as a rule present a semi-metallic appearance. The most general method for the formation of the nitrides is to heat a *chloride* of the respective element to redness in a current of dry ammonia; of the nitrides named, K_3N and Mg_3N_2 are the only ones which cannot be thus obtained. Of the bodies under consideration, those containing *basilous* metals (such as K, Mg, Zn, Fe) are easily recognised, as compounds of $(NH_2)'$ or $N,'''$ by the facility with which they are decomposed by dilute acids with elimination of their nitrogen as ammonium salt. The potassium compounds are readily decomposed by *pure* water. Those containing metals of which the oxides are reducible by *hydrogen* at a *red-heat*, when subjected to this operation, give off ammonia, with formation of metal. *All* nitrides and metal-amides, with the only exception of the *chromium compound*, when ignited with *soda-lime*, are decomposed into *ammonia* and metallic oxide.

III. *Oxides of Nitrogen.*

383. The monoxide N_2O ('laughing-gas') is a colourless gas of 1·524 sp. gr., which is very appreciably soluble in water; coefficient of absorption=0·778 at 15°. This oxide, being readily dissociable at a red heat with *evolution of heat*, supports combustion almost as well as oxygen does. It is however easily distinguished from this gas by its *not* acting on any of the many liquid reagents (alkaline pyrogallate, cuprous chloride, etc.,) which absorb free oxygen. It is not acted upon chemically by water or by solutions of even the strongest bases, although it is possible,* by the reduction of alkaline nitrites by means of sodium amalgam, to produce salts of a very feeble acid $NOH = \frac{1}{2}(H_2O + N_2O)$.

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* According to *Divers;* Chem. Soc. Journal for 1871.

384. The dioxide NO (nitric oxide) is a colourless gas of 1·038 sp. gr., which is only very sparingly soluble in water. This oxide is very stable, and its dissociation into $N_2 + O_2$ involves an absorption of heat; it accordingly does not support the combustion of ordinary combustibles—a lighted taper, for instance, is extinguished when plunged into the gas; but strongly heated phosphorus burns in it. Nitric oxide is easily distinguished from *all other gases* by the readiness with which it combines directly with ordinary *oxygen*, with formation of *red fumes* of the higher oxides N_2O_3 and N_2O_4. It is largely absorbed by concentrated solutions of *ferrous sulphate* or *chloride*, forming a *black* solution, from which the gas is easily expelled by boiling. When passed over nearly red-hot *soda-lime* along with *sulphuretted hydrogen*, it is converted into *ammonia*.

385. The trioxide N_2O_3 (the anhydride of nitrous acid HNO_2) can be produced synthetically from nitric oxide and oxygen, but is more conveniently prepared by the reduction, at a gentle heat, of *nitric acid* (of 1·2 – 1·3 sp. gr.) by means of *arsenious acid:* $H_2ON_2O_5 + As_2O_3 + 2H_2O = As_2O_5.3H_2O + N_2O_3$. It is a dark red-brown gas, condensible by intense cold into a blue liquid which boils somewhere about $-10°$. It dissolves freely in *concentrated sulphuric acid*. It is largely soluble in *water of* 0° with formation of a blue solution (of HNO_2 ?), which, when exposed to higher temperatures, evolves *nitric oxide*, while *nitric acid* remains in solution. The decomposition is the more complete, the more concentrated the solution and the higher the temperature. *Highly diluted* solutions of the acid are stable in the cold, and, according to *Fresenius*, can even be distilled without being at all largely decomposed; the acid accumulating in the first fractions of the distillate.

386. Metallic nitrites.—Nitrogen trioxide is readily absorbed by solutions of the hydrates of the alkalies and alkaline earth, with formation of nitrites $R'NO_2$ or $R''(NO_2)_2$; but it does not seem to be capable of decomposing the carbonates of these bases, nor does it act on any insoluble metallic oxides. The nitrites named can be produced also from the corresponding *nitrates*, by exposing these to a red heat, or by fusing them with metallic lead or other reducing agents, or by treating their solutions with nascent hydrogen. A number of *basic nitrites of lead* can be obtained by heating a solution of *nitrate* of lead with finely divided metallic lead, and from these basic salts the normal one $Pb\,(NO_2)_2$ can be prepared by treatment of their solutions with carbonic acid. From the alkaline, alkaline-earth and lead salts, a great variety of other nitrites have been prepared by double decompositions. Metallic nitrites are mostly crystalline salts, soluble in water, which, while stable up to 100° at least, are decomposed on exposure to a red heat into dissociated acid and metallic oxide. The least stable of all nitrites is the ammonium salt, $NH_4.NO_2$, which, when heated by itself or in its aqueous solution, breaks up, below 100°, into *nitrogen* and *water*. The potash and soda salts, on the other hand, are stable at a dull red heat; on prolonged exposure to higher temperatures they are reduced to *peroxides*. Examples of *sparingly soluble* nitrites are: the *silver-salt* $AgNO_2$, which, though readily soluble in hot water, requires 300 parts of cold water for solution; the *tetra-plumbic* salt $4PbO.N_2O_3.H_2O$, which dissolves in 34 parts of boiling and in 1250 parts of cold water; that double nitrite of K_2O and Co_2O_3, known as '*cobalt-yellow.*' (See § 153.)

387. *Reactions of Nitrites.*

1. Solid (or concentrated solutions of) nitrites when treated with cold dilute acids (SO_4H_2, HCl, $C_2H_4O_2$) are readily decomposed with evolution of *nitric oxide*, which, by the action of the air, is at once transformed into brown fumes of N_2O_4. When dilute solutions are mixed with

dilute sulphuric or other acid, a part at least of the liberated nitrous acid escapes decomposition, and the mixture then, in virtue of its containing free N_2O_3 (or NO_2H ?), exhibits the following reactions:

2. It readily **oxidizes** *hydriodic acid* (KI + free acid) into *iodine*, of which the least trace is easily recognised by means of starch or chloroform, as shown in § 308.

3. It **oxidizes** *sulphuretted hydrogen* into *sulphur* and water, the N_2O_3 being reduced to *ammonia*.

4. It **reduces** (and decolourizes) *acidified permanganate* to manganous salt.

5. It **reduces** dissolved *chloride of gold* and also *mercurous nitrate* to metal.

6. When added to a cold saturated solution of *sulphate* of *diamidobenzoic acid*, it produces an intensely coloured product, which from concentrated solutions separates out as a brown precipitate, but in dilute liquids remains dissolved with a *yellow* colour, which, after about a quarter of an hour's standing, has attained its maximum intensity. This (*P. Griess's*) test indicates as little as $\frac{1}{8}$ mgr. of N_2O_3 diffused throughout one litre of water.

7. When added to a large excess of concentrated *ferrous sulphate* solution, it produces a *black colouration*. (Comp. § 384.) This test holds also for neutral solutions of nitrites.

8. When the solution of an *alkaline nitrite* (or nitrate) is treated in the heat with *nascent hydrogen* in such a manner that the mixture remains alkaline to the end, the nitrogen is slowly, but at last completely, eliminated as *ammonia*. If the operation is conducted in a retort connected with a condenser, the ammonia passes into the distillate (along with water), and there, however little it may be, is easily detected by means of Nessler's reagent, or otherwise (§ 268). For the generation of hdyrogen within the nitrite solution the following combinations of reagents have been recommended: (*a.*) *Caustic fixed alkali* and *aluminium foil* (by the inventor of the method, *Schultze*); (*b.*) *Caustic fixed*

alkali, granulated *zinc*, and iron filings (*V. Harcourt*); (*c.*) *Tribe and Gladstone's* '*copper-zinc* couple'* and water.—(*Thorpe.*)

388. **The tetroxide** $N_2O_4 + xNO_2$ (peroxide of nitrogen), is a very volatile liquid, which at temperatures below 0° is colourless, but when heated beyond 0° becomes more and more intensely yellow, and at last orange-yellow, until, at 22°, it boils with formation of a dark red-brown vapour, which also is the more deeply coloured the higher its temperature. Towards water and bases this oxide behaves like a mixed anhydride of nitrous and nitric acids.

389. **The pentoxide** N_2O_5—the anhydride of nitric acid—forms colourless crystals, which melt at about 30°, and boil at about 45°. It is a highly unstable compound, being very prone, even at temperatures below its boiling point, to break up 'spontaneously' into oxygen and lower oxides. It readily unites with water to form nitric acid $HNO_3 = \frac{1}{2}(N_2O_5.H_2O)$.

390. **Nitric acid** HNO_3 is a colourless liquid of about 1·52 spec. grav., sufficiently volatile at ordinary temperatures to emit vapours which, on coming into contact with moist air, form dense clouds of less volatile higher hydrates. It boils at about 86°, with partial decomposition into oxygen and lower oxides of nitrogen which go off with the vapour of HNO_3, and water which mostly remains in the residue in the form of higher hydrates. On continued boiling this decomposition progresses slowly, but continuously, until—supposing the process to be conducted under the ordinary atmospheric pressure—the residue has come down in its composition to $HNO_3 + 1{\cdot}65H_2O$, which (mixed) hydrate then distils over unchanged at about 120°. This

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* *i.e.* Very thin sheet zinc, coated, by immersion in cupric sulphate solution, with a *thick* spongy layer of copper and *hydride of copper*, and freed from the mother liquor by careful decantation and washing with cold water. I have reason to believe that the 'couple' owes it efficacy, as a nitroxide reducer, mainly to the comparatively small quantity of hydrogen in the *copper-precipitate*, and not to the action of the couple on the water.—(*W. D.*)

hydrate contains 68°/$_0$ of real acid (HNO_3); its specific gravity is 1·414 at 15°·5. Highly-diluted nitric acid, when boiled down, first gives off pure vapour of water until the percentage of real acid in the residue has passed a certain limit value (which seems to lie somewhere about 8°/$_0$); the vapours then become more and more strongly acid, until at last they obtain the same composition $HNO_3 + 1·65H_2O$ as the residue. The real acid HNO_3 and its stronger hydrates have the power of dissolving the lower oxides N_2O_3 and N_2O_4, the more largely the less the quantity of water present beside HNO_3. Strong acid, largely charged with lower oxides ('fuming nitric acid'), possesses a brown colour; the dissolved oxides can be expelled by boiling; when the mixture is diluted, progressively, with water, it becomes, first green, then blue, and at last colourless, the oxides being gradually, and at last almost completely, decomposed into nitric acid and nitric oxide. Real, and sufficiently strong aqueous, nitric acid, especially if it contains lower nitrogen-oxides dissolved in it, behaves to a large number of substances as an energetic *oxidizing agent.** All solid elementary substances, with exception only of gold, platinum, and platinum-metals not palladium, when treated with nitric acid, are more or less readily oxidized. Sulphur, selenium, tellurium, phosphorus, arsenicum, antimony, tin, yield oxides or hydroxides, the *ultimate* products being: H_2SO_4, H_2SeO_3, TeO_2, H_3PO_4, H_3AsO_4, $Sb_2O_5 . 5H_2O$, meta-SnO_2, respectively. All ordinary metals, others than those just named, are, by the action of nitric acid, converted into nitrates. The kind of reduction which the nitric acid suffers in these reactions depends on the degree of concentration of the acid used, and on the nature of the substance acted upon. In most cases the reduction-products consist of nitrogen-oxides—nitric oxide being as a rule the most abundant; but in those cases in which the substitution of hydrochloric for nitric acid would have led to an evolution of hydrogen, a part at least of the nitrogen is converted into ammonia salt. Many lower oxides, and salts of lower oxides, are by the action of nitric acid converted into more highly oxygenated compounds; thus, for instance, *ferrous* salts are, in hot and sufficiently concentrated solutions, converted into *ferric* salts, with evolution of nitric oxide; *arsenious* acid is, under similar circumstances, converted into *arsenic* acid, etc. Strong nitric and *hydrochloric* acids, when heated together, decompose each other as follows: $HNO_3 + 3HCl = NOCl_2 + Cl + 2H_2O$. A mixture of the two acids ('aqua regia') consequently is capable of changing all metals, except iridium, into chlorides, an action which sometimes, as for instance in case of gold or platinum, is due only to the free chlorine, while in other cases the chloride $NOCl_2$ also contributes towards the chlorination.

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* *If 'nitric* acid' occasionally exhibits *reducing* properties, *e.g.* if found to reduce permanganic or chromic acid, this is a function of the *nitrous* acid present in the [illegible]urity.

Most combustible *carbon compounds*, when treated with strong aqueous nitric acid, are oxidized, some in the cold, others in the heat, with formation of lower oxides of nitrogen, organic pigments being generally converted into relatively colourless products. With a given substance, an oxidation is in general the more likely to set in, and to attain to complete combustion, the higher the temperature, the longer the action is allowed to go on, and the greater the excess and the degree of concentration of the acid employed. It is however to be observed that *real nitric acid*, HNO_3 (or a mixture of highly concentrated aqueous acid with oil of vitriol) when it acts in the cold on certain organic substances, produces other effects than (or besides) oxidation. Benzene, phenol, benzoic acid, and their homologues, for instance, when treated with the reagents named, are mainly converted into nitro-substitution-products, *i.e.* bodies not nitrates which contain per molecule, 1, 2,...xNO_2, where the original substance contained 1, 2,...xH. Glycol, glycerine, mannite, sugars and other di-, or more-atomic fatty alcohols are by the action of real HNO_3 (or of HNO_3

$+xH_2SO_4$) *in the cold* mainly changed into *nitrates.* Nitric acid is monobasic; it acts energetically on all basic oxides, hydrates and carbonates, with formation of nitrates.

391. Nitrates.—Normal nitrates are, most of them, crystalline salts, which readily dissolve in water, if they be not, like the mercurosum and bismuth salts, decomposed by water, with formation of insoluble basic salts. Nitrates are, as a rule, less soluble in aqueous nitric acid than in water, and some of them are practically quite insoluble in highly concentrated acid. Hence, certain substances, which are easily attacked by the aqueous, are not acted upon by the *real* acid. All nitrates, when strongly heated, are decomposed. The ammonium salt $NH_4.NO_3$ is stable in its aqueous solution, even at a boiling heat, but when heated by itself it first melts, and is then, at about 230°–250°, permanently decomposed into nitrous oxide and water. Of *metallic nitrates* proper, those of the alkali metals and of silver—all colourless salts forming anhydrous crystals $R'NO_3$—are the most stable. Their aqueous solutions can be evaporated to dryness without the salts suffering any decomposition, and the dry salts, when exposed to certain temperatures (which all lie considerably above 100°) melt into colourless liquids, which remain undecomposed even at temperatures situated considerably above their freezing points. But at about a dull red heat they begin to give up oxygen and to be reduced to *nitrites*, which in their turn, when very strongly heated, are reduced: the silver salt to metal, the rest to peroxides. Next after these monoatomic nitrates, in point of stability, come the nitrates of *barium, strontium, calcium, and lead*, which like the alkaline salts can be dehydrated in the heat, substantially at least, without decomposition, and require continued exposure to a red heat to be completely decomposed and reduced to oxides. The rest of metallic nitrates are all comparatively unstable compounds. Their solutions (or compounds with crystal water) as a rule cannot be dehydrated in the heat without loss of acid; and, when heated by themselves, they are all decomposed at or even below a dull red heat, the metals in general remaining in the form of the highest basic or neutral oxides stable at the respective temperatures. (Comp. §§ 31, 32, 183.)

392. Carbon, sulphur, sulphides, cyanides—in fact all sufficiently fixed combustible substances—when heated with solid alkaline or other nitrates (of sufficient stability) undergo combustion at the expense of the oxygen of the nitric acid. These processes are generally accompanied by a more or less violent deflagration, and sometimes also (as for instance when alkaline cyanide acts as combustible) by an explosion. Many other classes of salts, containing loosely combined oxygen (as chlorates, chromates, etc.), behave in this respect like nitrates.

393. *Reactions of Nitrates.*

1. Nitrates, when distilled with excess of *sulphuric acid*, are converted into sulphates with formation of a distillate of nitric acid, which, in absence of chlorides or other reducing agents, and if moderately dilute sulphuric acid is used, remains undecomposed. If *concentrated* sulphuric acid is used, the liberated nitric acid generally undergoes partial decomposition, with formation of brown-red fumes of N_2O_4. These fumes always make their appearance when a dry nitrate is decomposed by *fusion* (in a sublimation-tube) with *bisulphate of potash.*

2. Solid, or concentrated solutions of, nitrates when heated with concentrated *sulphuric acid* and *copper*, give off brown-red fumes of N_2O_4.

3. A dilute solution of (pure) nitric acid—or of a nitrate mixed with dilute sulphuric acid—does *not* liberate iodine from *iodide of potassium.*

4. Unlike many other oxidizing agents, such as chlorine, bromine, hypochlorous acid, etc., it does not destroy the colour of *indigo solution* in the cold, nor does it do so when

acting conjointly with *sulphurous acid*,—this distinguishes nitric from chloric acid,—but if the blue mixture is heated to ebullition, the colour quickly disappears. This reaction is very sensitive, and is rendered more sensitive still by the presence of chlorides; but it is not particularly characteristic, as many oxidizing agents, for instance ferric chloride, behave to indigo like nitric acid.

5. When a solution of a nitrate is mixed with its own volume of *concentrated sulphuric acid*, and, after cooling, a saturated solution of *ferrous sulphate* poured on the surface of the mixture, the nitric acid is gradually reduced to *nitric oxide*, which accumulates in the ferrous layer, and imparts to it a *black* or, in case of traces of nitric acid, a *rose-red* colour. This test is very delicate, but it obviously applies to *nitrites* also, which, however, differ from nitrates in this, that they colour the ferrous-salt solution even in absence of free acid, while, in the case of nitrates, the presence of a *very large excess of concentrated sulphuric acid*, *i.e.* the presence of $\mathbf{HNO_3}$ and the virtual absence of water, are essential conditions of success.

6. When even the most dilute solution of a nitrate is acidified, and then treated at a gentle heat with nascent hydrogen (for the generation of which finely divided *cadmium* or *amalgamated zinc* is best adapted), a part at least of the nitric acid is converted into nitrous acid, of which the least traces can be recognised, as shown in § 387, Nos. 2, 4, 6

7. The method given in § 387, under number 8, for the reduction of nitrous acid to *ammonia*, applies also to nitric acid, as the first effect of the reducing agents there named on a nitrate is to convert it into nitrite.

394. *Examination of a Solution of Inorganic Salts for Nitrites and Nitrates.*

There being no precipitants for nitrous or nitric acid *known*, these acids must be searched for by the application to separate quantities of the solution, of a proper combination of the tests given in §§ 387 and 393. A review of these tests at once shows that, even in absence of any foreign substances that might interfere with their application, they do not enable us to detect nitric in presence of nitrous acid. We accordingly begin by testing for *nitrites*. These, if present in sufficient quantity, are easily detected by the facility with which they are decomposed by even dilute sulphuric acid, with formation of ruby fumes of N_2O_4. (Test 1 in § 387). Lesser quantities can be recognised by their action—in neutral or slightly acid solutions—on ferrous sulphate (test number 7); the least traces: by the characteristic property of free nitrous acid of both reducing *permanganic* and oxidizing *hydriodic acid*, *i.e.* by tests 2 and 4; or else by means of *Griess's* reagent (test 6). We do not know to what extent this latter test may be applicable to complex solutions; in regard to tests 2 and 4, it is to be observed that, although both very delicate, they can in strictness serve only to determine the *potential* presence of nitrous acid. A solution containing ferrous and ferric salt, or arsenious and arsenic acids, for instance, behaves to both reagents as nitrous acid does. If the absence of such combinations as these cannot be conveniently proved, their influence may be eliminated by liberating the nitrous acid by means of acetic acid (in presence of much water), and separating it from the non-volatile parts by distillation. (Comp. § 385.) If the *distillate* gives positive indications with *both reagents*, it is almost absolutely sure to contain nitrous acid. If *nitrites* are proved to be *absent*, then *nitrates* may be searched for by the successive application to separate portions of the tests given under Nos. 2, 4, 5, and 6 in § 393.

395. Upon the behaviour of nitric and nitrous acid in alkaline solutions to *nascent hydrogen* (as explained in §§ 387-8 and 393-7) may be founded a very exact and almost absolutely general method for the detection of the two acids as a group. Add to the solution a large excess of *caustic soda or potash*, subject the mixture to distillation in a retort connected with a Liebig's condenser, and test the distillate for ammonia by means of Nessler's reagent. In case of a positive result, continue the distillation until the last trace of ammonia is expelled. Now add to the residue strips of *aluminium*, or granulated *zinc and iron* (and if necessary some water) and resume the distillation. Any nitrogen which *now* passes over as NH_3 must originally have been nitrous or nitric acid. This method applies to all nitrites and nitrates disintegrable by caustic potash.

396. *Analysis of Insoluble Nitrates and Nitrites.*

Most of these substances can be decomposed by boiling with excess of carbonate or hydrate of potash; the metals remain as insoluble carbonates or hydrates, while the acid passes into solution as potash salt. Cobalt-yellow (which is scarcely attacked by even *caustic* potash) is readily decomposed by caustic *soda* or *baryta*.

397. *Examination of Inorganic Nitrogen Compounds for Metals.*

Nitrates and *nitrites* offer no difficulty except that the free acids decompose sulphuretted hydrogen, and that their alkaline salts, on ignition, yield caustic alkali which attacks glass, porcelain, and platinum. If for one or the other of these reasons the presence of nitrates or nitrites should be inconvenient, they may be converted into chlorides by repeated evaporation with strong hydrochloric acid.

Of *metal-amides* and *metallic nitrides* the majority are easily decomposed by dilute mineral acids, with formation of metallic and ammonia salt. The few that are not attackable by dilute acids, can be disintegrated by fusion with *bisulphate of potash.*

398. *Organic Nitrogen Compounds.*

Under this heading we must content ourselves with showing how carbon compounds generally can be tested for nitrogen, and how ammonia, nitrous acid, and nitric acid can be traced through some of the most important classes of their more immediate derivatives. For these purposes nitrogenous carbides may be classified as follows :—

I. *Bodies more nearly related to* **Ammonia** :—
- **A.** Such as are connected synthetically with ammonia by
  - (1.) Reversible reactions.
  - (2.) Non-reversible reactions.
- **B.** Such which, though not *actual* ammonia derivatives, are compounds of the ammonia-residues N''', $(NH)''$, $(NH_2)'$.

II. *Bodies more nearly related to* **Nitrous** *or* **Nitric acid** :—
- **A.** True Nitrates or Nitrites.
- **B.** Nitro-substitution products and similar substances.
- **C.** Azo- and Diazo- Compounds.

Group I. A (1.) comprises the ammonium salts of organic acids and the amides, imids, amin-acids, nitriles (pseudo-cyanides), producible from these by abstraction of water. All these substances are decomposed, more or less easily, by aqueous caustic potash, with regeneration of *ammonia* and (salts of) the original acids. Examples : acetamide $C_2H_3O.NH_2$; oxamide $C_2O_2(NH_2)_2$; succinamide $C_2H_4(CO.NH_2)_2$; carbanide (urea) $CO(NH_2)_2$. Succinimide $C_2H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right\}NH$; carbimide (cyanic acid) $CO.NH$ or $NC.OH$. Oxamic acid $\left\{\begin{matrix}CO.NH_2\\CO.OH\end{matrix}\right.$. Aceto-nitrile $H_3C\text{-}CN$. Of the large number of genera belonging to

Group I. A (2.) the following may be named : (1) *amido-acids*, *i.e.* bodies like glycocol (amido-acetic acid) $CH_2(NH_2).COOH$; aspartic acid (amido-succinic) $C_2H_3(NH_2).(COOH)_2$. From *these* 'ammonia-acids' the ammonia *cannot* be regenerated by boiling with caustic potash ley—which distinguishes them from the *amine-acids.* A good example is the *asparagine*, which, as its formula $C_2H_3(NH_2)\left\{\begin{matrix}COOH\\CONH_2\end{matrix}\right.$ shows, belongs to both genera. When this substance is boiled with baryta water, only the NH_2 of the $CONH_2$ is eliminated as NH_3 ; with formation of aspartic acid. (2.) The so-called *compound ammonias*, bodies producible synthetically from ammonia by the replacement of $\frac{1}{3}$, $\frac{2}{3}$, $\frac{3}{3}$ of the hydrogen by its equivalent of alcohol-radicles. Of these ammonias, the '*monamines*' (the compounds NR'_3 of monovalent radicles, as ethyl C_2H_5, methyl CH_3, etc., with $(NH_2)'$, $(NH)''$ or N''') are the most important. These are all mono-acid volatile bases, more or less similar, chemically, and some of them even physically, to ammonia. Those in which $R=CH_3$ or $=(CH_3+nCH_2)$ are the less volatile, and also in other properties the further removed from ammonia, the greater n and the less of the original ammonia-hydrogen is left unreplaced. The 'tertiary' bases NR'_3 (for instance, triethylamine $NEt_3=N(C_2H_5)_3$) combine with the iodides IR' with formation of organic ammonium iodides, which, though undecomposible by caustic potash, can by the action of *water* and *oxide of silver* be converted into solutions of the corresponding hydrates $NR'_4.OH$, which are remarkable for the striking resemblance they exhibit (in the avidity with which they combine with acids, and act on metallic salts, and even in their action on animal tissues) to solutions of caustic soda or potash. Less similar to ammonia than the monamines, are the 'diamines' and the 'triamines,' bases derived from N_2H_6 and N_3H_9, respectively. *From no organic compound ammonia can NH_3 be regenerated by processes stopping short of a complete disintegration of the carbon groups*; at any rate, such processes, if they exist, have yet to be discovered.

All amido- (NH_2-) substitution products, although they may perhaps, on account of their containing carboxyl (COOH), be acids, possess, at least feebly basic properties. Thus, for instance, glycocol—although an acid—is, like NH_3, capable of uniting with hydrochloric acid. Most of the compounds of NH_2 which belong to I. A (1.) or (2.) when treated with water and *nitrous acid*, are decomposed in more or less exact accordance with the general equation: $\{\ldots NH_2+HNO_2=H_2O+\ldots(OH)+N_2\}$ the intra-radical (NH_2's) behaving like the extra-radical ones.

Group I. B comprises a large number of chemical genera; it includes, for instance, all *native* nitrogenous carbides: the 'alkaloids' (quinine, morphia, etc. etc.), the protein-substances (albumen, fibrine, etc. etc.), etc.

Group II. A.—The *nitrates* of organic bases proper are all readily decomposed into their constituents by treatment with aqueous hydrate or carbonate of potash, and consequently easily recognised as salts of nitric acid. The *nitrates and nitrites* of monoatomic *alcohols*, for instance nitrate and nitrite of ethyl, can be decomposed (the N_2O_3 compounds more easily than the N_2O_5 ones), by digestion in the heat (in sealed-up tubes) with aqueous *caustic alkalies*, into salts of their acids and the respective alcohols or ethers. The same decompositions can be effected more easily by means of *alcoholic* potash. These statements hold, in a limited sense, also for those nitrates of di- and poly-atomic alcohols which are generally denominated as nitro-bodies, such as nitro-glycerine, nitro-mannite, etc. All these alcohol nitrates and nitrites, when treated in alcoholic solutions with certain reducing agents, *e.g.* sulphide of ammonium, yield ammonia and the respective alcohols.

The *nitro-substitution* products (bodies containing nNO_2 instead of nH within their specific radicles) differ from nitrates in this, that they give up *no* N_2O_5 to caustic potash, and that, when treated with *reducing agents*—sulphide of ammonium, hydrochloric acid and tin, etc.—they yield *amido-bodies*, *i.e.* they exchange their NO_2's for NH_2's.

Most organic derivatives of nitric and nitrous acid are *explosive*, *i.e.* capable of burning at their own expense with evolution of heat. Some of them, *e.g.* Nitro-glycerine, are as explosive as gunpowder.

The bodies of group II. C are as yet of little practical importance. Suffice it to state that the diazo-bodies, being compounds of the radicle $-N=N-$, are highly unstable substances, and easily break up with formation of *free nitrogen.*

399. *Methods for the Detection of Combined Nitrogen generally*

may be deduced from the following facts; (1.) all *nitrides* which contain their nitrogen in a *non-oxidized* form (except one or two very refractory metallic nitrides proper and certain azo- and diazo-compounds) when burned in a combustion-tube with excess of *soda-lime*, give up the whole of their nitrogen as *ammonia.*

(2.) If the same operation is applied to organic compounds of *oxidized nitrogen* (bodies II., A and B, § 398) a part only of the nitrogen, if any, is evolved as ammonia; but the quantity of the latter can always be increased by adding to the substance a sufficient excess of *sugar* or other non-nitrogenous organic matter. The process, if thus modified, holds also for *inorganic* nitrates and nitrites.

(3.) All *organic nitrides*, without exception, when burned in a combustion-tube with *oxide of copper* or *chromate of lead*, —and all inorganic nitrates and nitrites when burned with *metallic copper*—give up their nitrogen mostly as such (N_2), and the rest as NO; hence, if matters be arranged so that the products, before leaving the tube, have to pass over a layer of red-hot *metallic copper*, the whole of the nitrogen is ultimately obtained as N_2, *i.e.* in case of carbon compounds as part of a mixture of N_2 and CO_2, of which the latter can be removed by means of *caustic potash* solution.

IV. PHOSPHORUS.

400.—I. *The 'Free Element'*

exists, at relatively low temperatures, in a number of allotropic modifications, which however, by the effect of heat, are all converted into the *same vapour* of the density $62 = P_4 : H_2$. If phosphorus vapour is cooled down suddenly it condenses into:

401. Ordinary phosphorus P_α, a colourless translucent solid of wax-like consistence, which melts at 44° and boils at about 250°. Spec. grav. = 1·8–2·1. This is the most inflammable of all elementary substances, the slight increase of temperature producible by gently rubbing it against a rough surface being sufficient to inflame it. When burned in an *excess* of oxygen or air, it is converted into dense white clouds of (solid) pentoxide with evolution of much heat, and of an intense white light. But if the phosphorus is in excess over the oxygen, trioxide is produced besides pentoxide. When exposed at the ordinary temperature to air, it undergoes slow combustion into teroxide and pentoxide, which at first assume the form of clouds, but soon settle, and, in presence of moisture, deliquesce into a syrup of aqueous phosphorous and phosphoric acids. This process of oxidation always induces the *transformation* of some of the ambient oxygen into *ozone*, which is one of the causes of the garlic smell observed during the process; it is also accompanied by the continuous evolution of a greenish-white light, which, however, can be seen only in the dark. Phosphorus is not soluble in, nor otherwise appreciably acted on by, water. It is slightly soluble in *ether*, in fatty oils, and in turpentine, and readily in *bisulphide of carbon*, from which solution it can be obtained in crystals belonging to the regular system. When exposed, under water, to sun-light, it undergoes gradual superficial conversion into a white opaque modification fusible somewhat above 44° into ordinary liquid P_α. When kept (in an inert atmosphere) at 230°–235°, or, at lower temperatures, brought in contact with a trace of iodine, it is converted into

402. Red (‘*amorphous*’) **phosphorus**, P_β—with evolution of 28246 units of heat for $P=31$ parts of substance. Red phosphorus is a red-brown, opaque, brittle solid of 2·1–2·2 spec. grav. which, when heated, remains apparently unchanged up to about 260°, when it is converted into ordinary phosphorus vapour P_4. Like P_α it is insoluble in water, but it is *not* dissolved by bisulphide of carbon or any of the other menstrua for P_α. In its chemical reactions it agrees with P_α in so far as the products formed by its action on a given reagent are the same as would have been obtained from the α-modification, but, containing far less internal heat than the latter, its reactions are not so easy to start, and when started, proceed more slowly. Thus, for instance, P_β does not get appreciably oxidized when exposed to the air at ordinary temperatures, and its kindling temperature is so high that it can be impunedly pounded in a mortar.

Reactions of Phosphorus P_α *and* P_β.

403. Hydrogen, Nitrogen, Carbon do not act chemically on phosphorus at any temperature.

Oxygen.—*Vide* supra.—Regarding the **halogens** see § 300.

Sulphur combines readily with phosphorus, with formation of P_2S_5, and in other proportions.

404. Metals (many) are capable of fusing together with phosphorus. The compounds are often (as in case of iron, nickel, cobalt, **platinum**) found to be more easily fusible than the metals themselves.

405. Aqueous acids.—Dilute *sulphuric* or *hydrochloric* acids are, under ordinary circumstances, not much acted upon by phosphorus. *Strong hydriodic* acid, when heated with phosphorus, yields phosphorous acid and a sublimate of hydriodate of phosphine. *Nitric acid*, especially in the heat, acts readily on phosphorus; the general result being the formation of a solution of phosphorous and phosphoric acids, in which the former is the more largely present the less the excess of oxidant. The action in the heat of an excess of amorphous phosphorus on dilute nitric acid, results in the formation of relatively much phosphorous acid and of some ammonia salt.—(*W. D.*)

406. Aqueous alkalies.—Phosphorus dissolves in boiling solutions of caustic alkalies or alkaline earths, with formation of gaseous phosphine and of hypophosphites. Ex.: $3Ba(OH)_2+P_8+6H_2O=3BaH_4P_2O_4+2PH_3$.

407. Heavy-metallic salts.—Gold, palladium, silver, copper, and some other of the less oxidizable metals, are precipitated, as such, from solutions of their salts, by the action of ordinary (or amorphous?) phosphorus, with formation of phosphorous or phosphoric acid.

II. *Hydrides of Phosphorus.*

408. Solid phosphoretted hydrogen (P_2H?).—Yellow flakes, insoluble in water. Takes fire at about 150°.

409. The hydride PH_2 forms a colourless, very volatile liquid, *spontaneously* inflammable in air, and imparting this property to even large quantities of other combustible gases (*e.g.* H_2, PH_3, etc.) when diffused through these in the form of vapour. When exposed to the light, or treated with aqueous *hydrochloric acid*, it is decomposed into the solid hydride and phosphine gas, the hydrochloric acid in the latter case suffering *no* permanent change.

410. *Phosphine* PH_3.—A colourless gas of 1·214 spec. grav. (air = 1), little soluble in water, and endowed with a nauseous smell similar to that of putrid fish. It readily takes fire and burns with a brilliant white flame into P_2O_5 (or PO_3H) and H_2O, but it is *not spontaneously* inflammable, unless contaminated with PH_2. Phosphine and *oxygen* when shut up together over water, slowly contract into phosphorous acid. Phosphine is quickly absorbed (and oxidized into phosphate) by *solutions of hypochlorous* acid or alkaline hypochlorites. It is readily decomposed by the solutions of certain heavy-metallic salts, *e.g.* by *cupric sulphate*, with formation of black flakes of Cu_3P_2; by *nitrate of silver*, with formation of a black precipitate of the approximate composition $Ag_2 + Ag_3P$, the O originally combined with the Ag_2 forming PO_4H_3; by *acetate of lead* or *mercurous nitrate*, with formation of brown flakes of (pure ?) metallic phosphide; by *chloride of gold*, with precipitation of pure metal. Phosphine does not act on litmus, nor exhibit basic properties towards aqueous acids, but it is capable of combining directly with *hydriodic acid* gas, with formation of a sublimable crystalline substance $HI.PH_3$, which by the action of water is readily decomposed into HI and PH_3.

411. Flame test.—A current of hydrogen contaminated with ever so little phosphoretted hydrogen or phosphorus vapour, when caused to issue from a *platinum* point, and kindled, yields a flame, the central cone of which exhibits a *green* colour, which becomes more intense when the flame is cooled down by a porcelain plate held in it. The spectrum of the flame is characterized chiefly by *two green lines.* This reaction is wonderfully delicate, and even if the flame is allowed to come in contact with glass, and thus to get discoloured by sodium, still presents a high degree of sensibility.

412. Metallic phosphides are solids which, when treated with mineral acids, are decomposed with formation of *phosphine gas* (and in general more or less P_2H and PH_2). Those of the more strongly electro-positive metals are decomposed by pure water.

III. *Inorganic Phosphorus Acids.*

Name.	Formula of	
........Acid.	Hydrogen Salt.	Anhydride.
Hypophosphorous, .	$PH_3O_2 = PH_2O.OH$, .	[P_2O, hyp.]
Phosphorous, . . .	$PH_3O_3 = PHO.(OH)_2$, .	P_2O_3.
Orthophosphoric, . .	$PH_3O_4 = PO.(OH)_3$, . .	P_2O_5.
Pyrophosphoric, . .	$2PH_3O_4 - H_2O = P_2O_7H_4$,	
Metaphosphoric, . .	$PH_3O_4 - H_2O = PO_3H$, .	

413. Hypophosphorous acid.—An aqueous solution of this acid can be obtained by decomposing a solution of the baryta salt (§ 406) with its exact equivalent of sulphuric acid, and removing the sulphate of baryta by decantation. The solution can be concentrated at temperatures not exceeding 105° without the acid suffering any decomposition. At 105° the greater part of the water can be expelled, and if what remains is cautiously concentrated, first at temperatures below 110° and ultimately at 130°—care being taken not to allow ebullition,—there remains at last an acid containing only 2°/₀ of water in the form of a syrup which, when kept in the cold, solidifies into a mass of large leaf-shaped crystals. The crystals melt at 17°·4.* Both the real, and highly concentrated aqueous acids, when heated over a flame, suffer decomposition into phosphine (free from PH_2) and orthophosphoric acid, thus: $2PH_3O_2{=}PH_3{+}PH_3O_4$. The acid is monobasic; it readily saturates bases. Most **hypophosphites** $PH_2O.OR'$ (where $R{=}1$ *equivalent* of metal), are crystalline salts, soluble in water. When heated for themselves over a flame they take fire, being decomposed in accordance with eq. $4PH_2O.OR'{=}2PH_3{+}H_2O{+}P_2O_5.2R'_2O$ (pyrophosphate). When boiled with *aqueous caustic potash*, they are decomposed thus: $PH_2O.KO{+}2HKO{=}2H_2{+}PO.(KO)_3$. The solutions of both the acid and its salts gradually absorb atmospheric oxygen, especially at higher temperatures.

414. Phosphorous acid.—The anhydride P_2O_3 is a white, readily sublimable solid. When heated in air it burns into P_2O_5. It acts violently on water, with formation of a solution of the acid. The **acid** can be obtained in the form of crystals (PH_3O_3), but is better known as a thick syrup soluble in all proportions in water. The aqueous acid, if dilute, is not changed by ebullition, but, if highly concentrated, is decomposed by heat into orthophosphoric acid and phosphine $4PH_3O_3{=}3PH_3O_4{+}PH_3$. It absorbs oxygen from the atmosphere with formation of orthophosphoric acid. Phosphorous is a stronger acid than hypophosphorous. It is dibasic. Phosphites generally are more stable than the corresponding hypophosphites. Their solutions do not get much oxidized on exposure to air; they are *not* decomposed when boiled with potash. When heated for themselves they are all decomposed with evolution of hydrogen, or of hydrogen and phosphine; fixed bases remain in combination with P_2O_5. Acid phosphites generally, and the normal *alkaline* phosphites, are soluble; the rest of phosphites are mostly insoluble or sparingly soluble in water.

415. In the examination of aqueous salt solutions, **hypophosphorous and phosphorous** acids, as a class, are easily recognised by the facility with which they are oxidized into phosphoric acid: (1.) By *chlorine* in the cold, both in acid and alkaline solutions. (2.) By *nitric acid*, in hot concentrated solutions. (3.) (In acid solutions in the heat) by *mercuric chloride*, with precipitation of calomel or metal. (4.) (The free acids) by free *sulphurous acid* in the heat—with evolution of sulphuretted hydrogen; or, if the reagent is in excess, *precipitation of sulphur*. (5.) By *nitrate of silver*, with formation of a black precipitate of metal. (This reaction succeeds better in ammoniacal than in acid solutions.) Of these reductions Nos. (3.) and (4.) are most characteristic, but none of them are conclusive unless proved to have involved the formation of phosphoric acid. If this acid should be present in the original liquid, it may be removed (from solutions of hydrogen or alkaline salts) by means of *magnesia mixture* (according to § 422), which, from dilute solutions at least, does not precipitate the two lower phosphorous acids.—The **discrimination** of the two acids is difficult. In absence of certain foreign substances it may be effected by means of *acetate of lead*, which does *not* precipitate hypophosphites, while from *neutral phosphites* it throws down a white lead salt, insoluble in acetic acid.

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* *Julius Thomsen;* Ber. der deutsch. chem. Gesellschaft, for 1874, p. 994.

416. A solution containing phosphorus in the phosphide, hypophosphite, or phsophite form, when treated with zinc and hydrochloric acid in a Marsh's apparatus, yields *phosphine* which goes off with the hydrogen, and can be recognised by the flame test given in § 411. The presence, in the gas, of H_2S, or AsH_3, or SbH_3 greatly interferes with the visibility of the reaction.

Phosphoric Acids.

417. The pentoxide P_2O_5 (the common anhydride of all phosphoric acids) is obtained by the combustion of phosphorus in excess of air or oxygen as a snow-white, very voluminous powder, sublimable at a red heat without decomposition, which, when exposed to moist air, immediately becomes 'sticky,' and soon deliquesces into syrupy hydrates. It combines with water with great avidity, and with evolution of much heat, exceeding in this respect even sulphuric acid (H_2SO_4). It has the power of abstracting water from almost all hydrates and pseudo-hydrates; even sulphuric acid and nitric acids when distilled with it are partially reduced to SO_3 and N_2O_5 respectively. If cautiously added to an excess of water at a low temperature, it dissolves as *metaphosphoric acid*, $P_2O_5H_2O = 2HPO_3$, which at low temperatures very slowly, but on ebullition very rapidly, takes up more water, and is converted into a solution of *orthophosphoric acid* $P_2O_5.3H_2O = 2PH_3O_4$. If the solution is evaporated below, and what remains dehydrated at, 160°, *this* acid remains, in the form of a stiff syrup, which when kept in a dry atmosphere solidifies very slowly into crystals. But if the process of desiccation is conducted at 215°, the pentoxide ultimately remains in the form of *pyrophosphoric acid* $P_2O_52H_2O = P_2O_7H_4$. This acid, when exposed to a red heat, loses water and ultimately leaves a residue of *metaphosphoric acid* HPO_3. The three hydrates are all very easily soluble in water. The pyro-acid solution behaves on standing and on ebullition exactly like the meta-one. Each of these three acids, although they are all three derived from the same anhydride, forms a distinct series of salts of its own.

418. *Orthophosphoric acid* is the best studied of the three phosphoric acids, and is the only one of which salts occur in nature; it is therefore often simply called 'phosphoric acid;' we adhere to this general custom, and consequently reserve the prefix 'ortho-' for cases in which its omission would produce ambiguity. *Phosphoric acid* is a strong *tribasic acid*, and accordingly forms three series of salts with the alkalies and with ammonia. Of these, the *dimetallic* salts $PO_4.R'_2H$ are obtained by adding to a solution of the acid a little more of hydrate or carbonate of alkali than is necessary for neutralizing its action on litmus, and evaporating to crystallization. From these salts $PO_4HR'_2$, the monometallic salts PO_4H_2R' and the trimetallic salts $PO_4R'_3$ may be produced by adding to their solutions the requisite quantities of, respectively, free acid or *caustic* alkali (not carbonate, because the salts $PO_4HR'_2$, although theoretically 'acid salts,' are not capable of decomposing carbonates). Of *Lithia and Oxide of Silver* only the salts Li_3PO_4 and Ag_3PO_4 are known. These two salts are insoluble, all other phosphates of mono-acid bases are soluble in water. Of the latter the majority can be obtained in crystals, which as a rule contain crystal-water. The diammonic salt $PO_4(NH_4)_2H$ is one of the few that form anhydrous crystals. With the basic oxides of di- or polyvalent metals phosphoric acid forms an immense variety of salts, of which the dimetallic, the trimetallic and the basic ones are all sparingly, if at all, soluble in water, while the comparatively limited class of monometallic salts are, as a rule, soluble in water.

419. *Behaviour of phosphates to heat.*—Phosphates containing ready formed water can as a rule be dehydrated at 100° or even lower temperatures. In this process the ammoniacal ones usually lose part of their NH_3 at the same time. A dull red heat generally suffices to send off the basic water and the ammonia, although the last remnants of these may require a bright red heat for being expelled. But in all cases the whole of the P_2O_5 and of the fixed bases ultimately remain as parts of a compound which, according to the proportions of these two constituents to each other, is a meta-, a pyro-, or an orthophosphate. This phosphate however needs not necessarily be identical with the one originally present, potentially, in the salt, as oxidizable oxides, such as FeO, may have suffered oxidation by atmospheric oxygen. Pure ammonic phosphates leave residues of metaphosphoric acid. Mercury-phosphates in general lose oxygen and metal, and there remains ultimately some compound of $P_2O_5 +$ Mercury-oxides (metaphosphate ?).

420. The following is a **list** of practically important **phosphates**:— Ordinary *phosphate of soda*, large crystals of comp. $Na_2HPO_4+12H_2O$. *Microcosmic salt*, crystals of comp. $Na(NH_4)HPO_4+4H_2O$. *Monopotassic salt*, large crystals of comp. KH_2PO_4; stable up to 400°. The *dipotassic* salt does not crystallize. *Tricalcic salt* ca_3PO_4 forms the main constituent of bone-ash, and occurs in nature as phosphorite. Compounds of this salt and chloride of calcium occur native as *Apatites* $6ca_3PO_4.CaCl_2$ (the Cl being as a rule partially and sometimes wholly replaced by fluorine). The tricalcic salt dissolves in mineral acids as '*superphosphate*,' which can be obtained in crystalline scales $caH_2PO_4+H_2O$, soluble in water; solution strongly acid. The normal *alumina salt* is obtained when alum-solution is added to an excess of ordinary phosphate of soda, as a white gelatinous precipitate, insoluble in acetic acid. Occurs native as *Gibbsite* $Al_2O_3P_2O_5.4H_2O$ and as '*Rotondo-mineral*' (formula ?), which latter forms large deposits on certain islands in the West Indies. The *triplumbic salt* pb_3PO_4, as obtained by double decompositions from solutions, is a white powder, fusing on charcoal before the blowpipe into a clear heat, which, on cooling, freezes into a crystal. Occurs native as a constituent of *Pyromorphite* $6pb_3PO_4.PbCl_2$. [pb, ca $=\frac{1}{2}$Pb, $\frac{1}{2}$Ca].

Reactions for the Detection of Phosphoric Acid.

421. (a) *In Solids.*

Most anhydrous metallic phosphates, when intimately mixed with *carbonate of soda* and *lampblack*, and then fused together (in narrow sublimation tubes) with *sodium* or *magnesium* at a red heat, are reduced with formation of the *phosphides* of these metals, which can be identified as such in Marsh's apparatus (as shown in § 416), or by their giving off a smell of phosphine, when moistened with water.

Most phosphates when moistened with strong *sulphuric acid* and then exposed to the inner cone of an oxidizing blowpipe flame, impart to the outer portions of the flame a characteristic, but rather transitory, bluish-green colour.

422. (b) *In purely aqueous solutions of alkaline phosphates.*

(1.) *Nitrate of silver* gives a yellow precipitate, which always consists of the trimetallic salt PO_4Ag_3 even if the salts $PO_4R'H_2$ or $PO_4R'_2H$ be used. This silver salt being soluble in nitric acid, and also in large quantities of nitrate of ammonia, the precipitation is complete only in case of the trimetallic salts of potassium or sodium.

(2.) *Chloride of calcium* (from the trimetallic salts, which, if necessary, must be produced by addition of ammonia) precipitates the whole of the P_2O_5 as $Ca_3(PO_4)_2$,—a white gelatinous precipitate, insoluble in water, slightly soluble in ammonia salts, easily soluble in nitric, hydrochloric, and in acetic acid. *Chloride of barium* behaves similarly, but is not so characteristic a reagent.

(3.) *Sulphate of magnesia*, when added to solutions of the salts PO_4R_2H of the alkali metals, produces a slow-forming precipitate of $PO_4MgH.7H_2O$; in the heat, or if a trimetallic salt be used, a powdery precipitate of $(PO_4)_2Mg_3.5H_2O$ is produced somewhat more readily. Neither reaction is very sensitive; but, if instead of pure magnesium salt,

(4.) *Magnesia mixture** be used as reagent, and a sufficient quantity of *caustic ammonia* added at the same time (there should be at least three parts of free NH_3 in every 100 of mixture), then, even in dilute liquids, a crystalline precipitate of the double phosphate $PO_4MgNH_4.6H_2O$ is produced, in which gradually the whole of the phosphoric acid accumulates. (Comp. § 237.)

Note.—All these reactions come out with *arsenates* as well as with phosphates, except that the silver salt AsO_4Ag has a brown (instead of a yellow) colour, and that the precipitates in case of (2.) and (3.) may differ in constitution from the corresponding phosphate ones.

423. (c) *In solutions of phosphates of protoxides* R'_2O *or* $R''O$ *in nitric acid.*

(5.) An excess of *nitrate of bismuth*, when added to such a solution, precipitates the phosphoric acid completely in the form of a white powdery salt $P_2O_5.Bi_2O_3$ insoluble, even in the heat, in water, and in dilute nitric acid; while the bases remain in solution as nitrates. If alumina or ferric oxide are present, these are precipitated partially along with the phosphoric acid. The reagent should not contain any more free nitric acid than is necessary to prevent its being precipitated by addition of pure water. Such a solution, however, is precipitated by chlorides; hence the reaction is not applicable in presence of appreciable quantities of chlorides. Sulphates also interfere with it.

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* A mixed solution of sulphate—or, what is better, chloride—of magnesium and sal-ammoniac ($MgCl_2 : 2NH_4Cl$) in dilute ammonia.

424. (d) *In nitric solutions of phosphates of any kind.*

(6.) If such a solution is added to a large excess of one of *molybdate of ammonia* in nitric acid* (which must contain *at least* 30 parts of MoO_3 for every one of P_2O_5 present), the whole of the phosphoric acid is, after some time in the cold, but more readily on heating, precipitated in the form of yellow crystalline powder of the approximate composition $10MoO_3.PO_4(NH_4)_3$, which, though slightly soluble in water, and easily soluble in caustic ammonia, and in excess of phosphoric acid, is quite *insoluble in the reagent* and insoluble also in moderately strong solutions of nitrate of ammonia, even in presence of free nitric acid. The precipitate therefore must be washed with one of the two liquids named, not with water. The bases remain in solution as nitrates. From the ammonia solution of the precipitate the phosphoric acid can be precipitated by means of magnesia mixture. (See No. 4.) In presence of *chlorides* the reaction loses much of its sensibility, and may even fail altogether.

Arsenic acid behaves to the molybdate like phosphoric;

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* 100 grms. of molybdic acid are made into a milk with 200 grms. of water and dissolved by gradual addition of the least sufficient quantity of strong ammonia; and this solution is then poured into 1250 cc. (=1500 grms.) of nitric acid of 1·2 spec. gravity. The mixture is allowed to stand in a warm place for twenty-four hours to allow any phosphoric acid that may be present to separate out, and then decanted off the precipitate.

only the precipitate requires a temperature of at least 40° C. for its formation. *Silicic acid* causes a yellow colour, similar to that produced by traces of phosphoric or arsenic acid, but forms *no* precipitate. The only acids which, in the application of this test, are liable to be mistaken for orthophosphoric acid are pyro- and metaphosphoric acids; these two being, by the action of nitric acid in the heat, gradually converted into the ortho-acid. *Arsenic acid* is, of course, easily distinguished and separated from phosphoric by means of *sulphuretted hydrogen.* (Comp. § 46.)

425. *Separation of Phosphoric acid from Bases.*

From the solution of a mixed phosphate—which, for the sake of generality, we will assume to have been prepared with nitric acid, and to actually contain all the bases to be named,

Silver, *mercurosum*, and as a rule part of the *lead*, can be precipitated in the usual manner by means of hydrochloric acid; and from the filtrate, after removal of the nitric acid by repeated evaporation with hydrochloric acid, what is left of

Metals of the *copper or arsenic group* can be completely precipitated by means of *sulphuretted hydrogen.* The phosphoric acid passes into the filtrate along with the metals of the iron, barium, magnesium, and potassium groups. If such a filtrate should contain no other metals than Fe, [Cr ?] Ni, Co, Mn, Zn, these may be precipitated, and separated from the phosphoric acid, by addition of excess of ammonia, sal-ammoniac, and sulphide of ammonium. If the mixture contain an excess of the latter reagent, and be kept at a gentle heat for some time previous to filtration, the whole of the phosphoric acid passes into the filtrate as ammonium salt. If, however, the solution contains alumina, magnesia, lime, baryta, strontia, then these bases are precipitated by the reagents named as phosphates; and the precipitate obtained consequently may possess a very complex composition. Hence, in the general case, it is better, after removal of the copper and arsenic groups, to begin by peroxidizing the iron, and then—after due concentration—to precipitate the

Barium, strontium, and calcium, by means of sulphuric acid* and alcohol (according to §§ 200 *et seqq.*, 225), and to examine the filtrate, after removal of the alcohol by evaporation, for the rest of the metals, as shown in §§ 200 *et seqq.*, and in §§ 281 *et seqq.* The detection of phosphoric acid in such a filtrate, as in fact in any solution freed by means of sulphuretted hydrogen from copper group and arsenic group metals, offers no difficulty. We need only eliminate what can be precipitated by means of sulphide of ammonium, and search for phosphoric acid: in the filtrate by means of magnesia mixture, in the nitric solution of the precipitate by means of molybdate of ammonia.

Special methods

for the separation of phosphoric acid from certain groups of bases may be founded upon the following data:—

426. By fusion with excess of carbonate of soda the phosphates of all the metals of the *iron group* (except **aluminium**) and of magnesium can be completely decomposed into (soluble) alkaline phosphate and (insoluble) metallic oxide or carbonate. The phosphates of Al_2O_3, (Ba, Sr, Ca)O are *not* decomposible in this manner.

The phosphates named as being decomposible by fusion with carbonate of soda, when given as recently formed precipitates, can be decomposed likewise by continued boiling with *caustic* potash or soda, or even with carbonate of alkali solution.

427. Separation of Phosphoric acid from the **oxides of the iron group** (except alumina) and of the **barium** and

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* The same reagents may serve to separate phosphoric acid from lead.

magnesium groups. Ferric (and aluminic) phosphates are insoluble in *acetic* acid, while the recently precipitated phosphates of barium, strontium, calcium, magnesium, manganese are soluble in this menstruum. A dilute solution of *ferric* (aluminic) acetate, if not too strongly acid, is completely decomposed by boiling into a precipitate of basic acetate of the base and a solution of acetic acid. If the solution contained ferric phosphate (which is appreciably soluble in ferric acetate) this salt is on boiling precipitated along with the basic acetate. Upon these facts may be founded the following method of separation which will frequently be found useful, especially in the analysis of native phosphates, of the ashes of plants, and other mixtures containing phosphates. The substance is dissolved in hydrochloric acid, the iron peroxidized by means of nitric acid or chlorate of potash and the excess of free acid removed as far as possible by evaporation. The residue is then diluted largely with water and an excess of solid *acetate of soda* dissolved in the liquid. All that is potentially present of ferric (and aluminic) phosphate is thereby precipitated in the form of a yellowish gelatinous mass. If the iron predominates over the phosphoric acid, the mixture assumes the brown red colour characteristic of ferric acetate, and some of the phosphate of iron remains dissolved. Should this colour not show itself, ferric chloride must be added until the mixture is intensely brown-red. All these operations must be done in the cold. The mixture is then boiled, filtered in the heat, and the precipitate washed with hot water. The precipitate contains *all the iron* (all the alumina) and all the phosphoric acid; the protoxides (MnO, BaO, CaO, MgO, etc.) pass into the filtrate. (Comp. § 206.)

428. Tin method.—Upon the fact that metastannic acid when formed by the action of nitric acid on tin in presence of phosphoric acid, unites with this acid into a compound insoluble in nitric acid, *Reynoso* has founded a method for the analysis of phosphates which is of very general applicability. The substance is brought into solution by means of nitric acid. Certain native phosphates are not readily disintegrable by nitric acid; these must be decomposed by means of hot concentrated hydrochloric acid, and from the solution the hydrochloric acid be expelled by repeated evaporation with strong nitric acid. This having been done, a quantity of metallic tin—which should amount to about eight times the weight of P_2O_5 present—is placed in the acid liquid, and the whole digested until the metal is completly oxidized. The mixture is then diluted, allowed to settle, and filtered. The filtrate contains all the bases as nitrates—except small quantities of Fe_2O_3 and Al_2O_3, which, as a rule, are carried down by the oxide of tin along with the phosphoric acid. To analyse the precipitate $[SnO_2+xP_2O_5+y(Fe_2O_3, Al_2O_3)]$ it is dissolved in caustic potash, the solution saturated with sulphuretted hydrogen (when the Al_2O_3, Fe_2O_3 are precipitated, the Al_2O_3 as phosphate) and filtered. From the filtrate the phosphoric acid is precipitated by means of magnesia mixture.

429. *Pyrophosphoric acid* $P_2O_5 2H_2O$.—(Regarding mode of formation see § 417.) A solution of this acid in water, like that of the ortho-acid, does *not* coagulate *albumen*. When neutralized with an alkali, it gives white precipitates with chloride of *barium*, chloride of *calcium*, nitrate of *silver*. *Sulphate of magnesia* gives a white precipitate $P_2O_7Mg_2$ soluble in excess of reagent, and in excess of alkaline pyrophosphate. From the solution the magnesia salt is re-precipitated on boiling, but not on addition of *ammonia*. *Molybdate of ammonia* (in nitric solutions) gives no immediate precipitate in the cold; on standing, the pyro- is changed into the ortho- acid, which then precipitates the reagent.

430. *Metaphosphoric acid* $P_2O_5H_2O$.—(Comp. § 417.) An aqueous solution of this acid coagulates albumen. When neutralized with an alkali, it gives with nitrate of silver a white precipitate of the composition $AgPO_3$. The neutral solution is *not* precipitated by *magnesia* mixture. *Molybdate of ammonia* behaves to this as it does to the pyro-acid.

431. *Metallic Anorthophosphates.*—The two hydrates $P_2O_5H_2O$ and $P_2O_5 2H_2O$ serve as the starting-points for the preparation of at least eight distinct classes of anorthophosphates, each of which corresponds to a particular typical anorthophosphoric acid. The reactions of these different acids are as yet little understood. All we can afford to state here is that anorthophosphates, whether viewed as derivatives of the respective *bases* or as derivatives of the hydrates from which they were *prepared*, present endless anomalies. They are however easily enough identified as compounds of P_2O_5, as they can all, either by prolonged heating with mineral acids, or, if this method fails, by fusion with excess of alkaline carbonate, be converted into orthophosphates, and analysed as such.

432. Of *Organic Phosphorus Compounds*

the following may be named :

(1.) **Compound phosphines :** substances derived from PH_3 or nPH_3 by the substitution for 1, 2 ... equiv. of an alcohol radicle for 1, 2 ... atoms of hydrogen. These organic phosphines are all strong bases, analogous in their reactions to the corresponding NH_3-derivatives. The best known phosphines are : Triethylphosphine $P(C_2H_5)_3$ and trimethylphosphine $P(CH_3)_3$: both colourless, volatile liquids, insoluble in water, but soluble in aqueous acids, with formation of stable salts, *e.g.* $P(C_2H_5)_3.HI$. Like the corresponding nitrogen-bases they unite with the iodides R′I (where $R'{=}CH_3$, C_2H_5...) into phosphonium-iodides (ex. : $P(C_2H_5)_4I$) which, when treated with water and oxide of silver, yield solutions of the strongly basic hydrates $PR'_4.OH$. A point in which they differ from monamines is the facility with which they unite directly with ordinary oxygen into oxides of the composition $PR'_3.O$.

(2.) **Phosphorous** and **phosphoric** ethers, *i.e. phosphites* and *phosphates* of methyl-, ethyl-, etc., alcohol. Each of these alcohols forms three phosphites and phosphates, viz. :—

Phosphites.	Phosphates.	
. . . .	$PO.(OH)_3$	3-basic.
$(POH).(OH)_2$ . . . $POR'.(OH)_2$	. . . . . . $PO.(OR)(OH)_2$ . .	2-basic.
$POR'.(OR')OH$ . .	$PO.(OR')_2OH$ . . .	1-basic acids.
$POR'.(OR)_2$ . . .	$PO.(OR')_3$	Neutral Ethers.

All these organic phosphites and phosphates when heated with water—and their salts when heated with dilute mineral acids—are more or less readily resolved into their respective alcohols and PO_3H_3 or PO_4H_3.

(3.) The so-called **protein-substances** (albumen, fibrine, caseine, etc.) all contain phosphorus, part of which is, in general, present as phosphate, while the rest forms part of organic radicles.

All organic phosphorus compounds when treated in the heat with concentrated *nitric acid*, which, in the case of volatile substances, should be done in sealed-up tubes—are changed so that the phosphorus is either converted into orthophosphoric acid, or at least into some compound phosphoric acid, which, when fused, as alkali-salt, with alkaline nitrate, is converted into orthophosphate.

433. *Summary.*

All phosphorus compounds, not salts of P_2O_5, when treated with the proper kind of oxidizing agent, are converted into *orthophosphate.* A complete oxidation can always be effected by the action at a red heat of a mixture of alkaline nitrate and hydrate or carbonate.

Metallic **anorthophosphates** when fused with alkaline carbonate, have their phosphorus converted into *orthophosphate.*

Phosphides, hypophosphites, phosphites, if decomposible by dilute acids, can be distinguished from phosphates by their giving *phosphine*, when treated with nascent hydrogen. (See § 416.)

Aqueous solutions of **hypophosphites** and **phosphites** can be recognised by their power of reducing aqueous nitrate of silver, mercuric chloride, sulphurous acid (and other agents), with formation of *orthophosphoric acid.* *Magnesia mixture* precipitates neutral *orthophosphate*, but does not precipitate the salts of the two lower oxides.

V. BORON.

434. Elementary Boron (as prepared by the decomposition of fluoride of boron gas (BoF_3) with potassium at a red heat) forms an olive-brown powder, which, in absence of air, can be heated to whiteness without fusing. When heated in air, it burns mostly into trioxide (Bo_2O_3), the rest into nitride of boron. Boron does not decompose (liquid) water, but is slightly soluble therein. It is insoluble in solutions of ordinary salts. *Nitric acid* converts it into boracic acid. The oxidation of boron into its trioxide can also be effected by fusion with hydrate, carbonate, acid sulphate, or nitrate, of fixed alkali. Boron when heated in chlorine is converted into the chloride $BoCl_3$. There is another allotropic modification of boron, called **adamantine boron** on account of its similarity in physical properties to diamond. Such adamantine, like ordinary, boron burns in chlorine, but it is scarcely oxidizable by nitric acid, nor even by fused nitre. What was formerly called '*graphitic boron*' is boride of aluminium $AlBo_2$.

435. Boric oxide Bo_2O_3 (Syn. Boric anhydride; anhydrous 'boric acid') is a colourless solid, fusible below a red heat into a viscid liquid, which on cooling hardens into a colourless transparent glass. Boric oxide, although when heated for itself it proves perfectly fixed at a red heat, and volatilizes only at an intense white heat, is very appreciably volatilized even at (and perhaps below) the former temperature, when at the same time exposed to a current of steam, and still more so in alcohol-vapour. The fused oxide readily dissolves metallic oxides with formation of borates, and when fused together with salts of more volatile acids with fixed bases, expels these acids (Ex.: $K_2ON_2O_5 + Bo_2O_3 = K_2OBo_2O_3 +$ dissociated N_2O_5). It readily dissolves in hot water with formation of

436. Boric acid (Syn. Boracic acid), which on cooling separates out in the form of scales of the composition $Bo_2O_3.3H_2O = 2Bo(OH)_3$, possessing a mother-of-pearl lustre and a fatty feeling. The crystals dissolve in about 25 parts of cold water. The solution behaves like a weak aqueous acid; it colours blue litmus solution wine-red; it acts on alkaline hydrates, but does not neutralize completely their action on litmus; it decomposes alkaline carbonates. But the borates formed can be partially re-decomposed by excess of carbonic acid. The aqueous acid has the singular and characteristic property of colouring (yellow) *turmeric paper* brown-red; the colour becomes more intense on drying. When the solution is evaporated, and especially when it is *boiled* down, a considerable portion of the acid volatilizes with the steam. Both the acid and its anhydride dissolve in *alcohol;* the solution when kindled burns with a characteristic *green* flame, and when boiled down yields vapours which are even richer in Bo_2O_3 than those formed from the aqueous solution.

437. Borates.—Boric acid is of variable basicity, and consequently forms a great variety of salts with basic oxides. With *soda* it forms at least three distinct salts, viz.: the normal borate $Na_4Bo_4O_8+16H_2O$; 'Borax,' $Na_2H_2Bo_4O_8+9$ or $4H_2O$; the triacid borate $NaH_3Bo_4O_8+7H_2O$. Alkaline borates are readily soluble in water; the solutions are alkaline to test-paper. Most other borates are difficultly soluble, but none are quite insoluble, in water; hence there is no sensitive precipitant for borates. The solutions of all borates, except the more basic potash and soda salts, lose some of their acid on evaporation. The best known of all borates is

Borax.—This salt forms two crystalline hydrates. When a solution saturated above 79° is allowed to cool slowly, then between 79° and 56° it deposits *octahedral* crystals of $Na_2O.Bo_2O_3+5H_2O$, while the mother liquor (from 56° downwards) deposits *prismatic* crystals belonging to the monoclinic system, of 'ordinary borax' $Na_2O.Bo_2O_3+10H_2O$. The octahedral crystals are stable, the prismatic ones effloresce, in dry air. Either hydrate, when heated, readily melts in its crystal water, which on further heating is expelled, and, on account of the viscidity of the melted salt, the anhydrous salt remains as a very voluminous, spongy mass. This mass ('calcined borax') fuses at a red heat into a viscid liquid which, on cooling, hardens into a colourless transparent glass. That the anhydride when in the state of fiery fusion, has the power of dissolving metallic oxides with formation of borates which, in general, are soluble in the excess of 'borax-glass,' must be supposed to be known to the student. 100 parts of water dissolve at 20°, 7·9 parts, and at 90° 120 parts of *ordinary* borax. Moderately strong solutions behave to reagents as follows: *Nitrate of silver* gives a white precipitate of borate of silver. When the solution is diluted sufficiently with water, the salt undergoes dissociation and the dilute liquid now precipitates from the reagent brown oxide of silver. *Nitrate of lead* gives a white precipitate soluble in excess of the reagent. *Chloride of barium* gives a white precipitate soluble in excess of reagent and also in sal-ammoniac. These three precipitates are soluble in dilute nitric acid. *Hydrochloric acid* (excess) produces free boric acid, which from *concentrated* solutions may partially separate out in crystals. In dilute solutions, the presence of free boric acid can be demonstrated by means of turmeric paper, which, when soaked with the acid mixture, at first remains unchanged, but on being dried on a warm porcelain plate soon assumes the red-brown colour characteristic of boric acid. This test is very sensitive, and in a high degree characteristic; of all oxides which can possibly be present in an *alkaline* solution of alkaline salts, the only one which acts on turmeric like boric acid is *zirconia*, an oxide of very rare occurrence. All these tests apply also, substantially, to other alkaline borates than borax.

438. Flame-tests.—*Any solid borate* when mixed with its own weight of *fluor-spar* and 4·5 times its weight of *bisulphate of potash*, and then exposed to the blue cone of an oxidizing blowpipe flame, imparts to the outer flame the green colour characteristic of glowing Bo_2O_3. Most borates when mixed with concentrated *sulphuric acid* yield free boracic acid, which on addition of *alcohol* dissolves. The solution consequently, when kindled, burns with a flame which, at the edges at least, exhibits the green boron-colour. The colour is best seen when the flame, after having been blown out, is re-kindled. Whether the one or the other of these flame-tests be adopted, a positive result is decisive only if all foreign substances which are capable of producing a green flame-colour are proved to be absent. The following is a list of these substances:—Haloids of *copper*, *thallium*-salts, *tellurous* oxide, *baryta*-salts (especially the chloride), *molybdic acid*, *phosphoric acid*, *chloride of ethyl*. (This ether is always produced in the case of the alcohol test, when the substance contains chlorides.)

439. For the **detection of boric acid** in a complex mixture of salts, the most generally applicable method is, after removal of the copper and arsenic group metals by means of sulphuretted hydrogen, to precipitate in the heat with excess of *carbonate of soda*, to filter, and to the filtrate to apply the *turmeric-paper* test. The volatility of boracic acid with vapour of water and of alcohol (which creates such difficulties in quantitative analysis) in qualitative analysis, might perhaps be advantageously applied for the concentration of small quantities of the acid diffused through a mass of foreign salts. The correct *modus operandi* probably would be to decompose the salts with concentrated sulphuric acid and, after addition of enough of water for rendering any hydrochloric or nitric acid that might be present non-volatile, to subject the mixture to a prolonged distillation; replacing from time to time the water that has distilled over. If the distillate contained hydrochloric or nitric acid, these might be removed by re-distillation with enough of sulphate of soda to fix these acids by means of the reaction $Na_2SO_4+H(Cl \text{ or } No_3)=NaHSO_4+Na(Cl \text{ or } NO_3)$. The purified distillate, if supersaturated with soda and then evaporated to dryness, would furnish part at least of the boric oxide originally present in a concentrated form.

VI. SILICON.

440. *The 'Free Element'*

exists in three allotropic modifications. **Amorphous Silicon,** as prepared by decomposing fluosilicate of potassium with metallic potassium in the heat (*i.e.* by realizing the reaction $SiF_6K_2 + K_4 = 6KF + Si$), and extracting the fluoride of potassium by means of water—is a dull brown powder soiling the fingers, heavier than water, which does not attack it, even on boiling. It is not acted on by nitric or sulphuric acid, but readily dissolved by hot *caustic potash ley*, as also by aqueous hydrofluoric acid, with formation of alkaline silicate, and of fluoride of silicon, respectively. When heated in *chlorine* it is transformed into *chloride of silicon*, a volatile liquid, boiling at 50°. When heated in *air* it burns into *silica* SiO_2. When heated in an inert atmosphere, it at first shrinks greatly and assumes a darker colour, and at last, at a white heat, melts; and when subsequently allowed to cool it hardens into a steel-grey metallic-looking mass. Strongly heated silicon seems to be chemically identical with

Graphitoidal Silicon.—When *aluminium* is saturated with silicon at high temperatures and then allowed to cool, this modification of silicon separates out in crystals, which can be isolated by dissolving away the aluminium with hydrochloric acid. Graph. Si forms graphite-like shining hexagonal tables of spec. grav. 2·49. By the action on aluminium, kept fused at a very high temperature, of hydrogen and chloride of silicon can be produced

Adamantine Silicon.—Iron-grey iridescent crystals, derived apparently from the rhombic octahedron, and, like diamond, often exhibiting curved faces. The crystals are hard enough to scratch glass. The crystalline modifications differ from the amorphous one mainly by their lesser chemical activity.

Graphitoidal and fused silicon at least can be heated even to whiteness in pure oxygen without burning, and do not dissolve in any acid except in nitro-hydrofluoric.

441. *Silica* SiO_2

occurs abundantly in nature, both for itself and in combination with metallic oxides, as '*silicate.*' The numerous minerals which consist substantially of free silica may be divided into the following classes:

(1.) *Crystalline Silica* (ex., quartz, rock-crystal, amethyst, etc. etc.) This modification forms resplendent, transparent, hexagonal crystals (mostly combinations of the hexagonal prism with the pyramide), which are harder than glass, but less hard than corundum. Spec. grav. 2·5 to 2·8. There is a particular modification of native crystalline silica, called

(2.) *Tridymite*, which differs from the ordinary forms (1.) mainly in its specific gravity, which lies about the value 2·3.

(3.) *Amorphous Silica* (ex. Opal).

Less hard than the crystalline forms; spec. gr. 1.9–2.3.

Flint, *carneol*, and certain other varieties of native silica, are mixtures of the ordinary crystalline, and of the amorphous, modifications.

Artificially, silica can be prepared in various ways, for instance by the dehydration of any of the hydrates (q. v.) by the aid of heat, when it remains in the form of a white amorphous very voluminous powder, which when heated is very mobile and flows almost like a liquid.

Silica is absolutely non-volatile, and does not fuse at even the highest temperatures producible by means of a blowpipe flame or an ordinary furnace. In an oxyhydrogen flame, however, it melts into a colourless and transparent viscid glass.

At high temperatures, and in opposition to most non-volatile metallic oxides and their compounds with water or volatile oxygen-acids, silica behaves as a powerful acid-anhydride. With most of these oxides it is capable of uniting in a great variety of proportions into 'silicates,' and these are mostly fusible; hence, although real silica is absolutely infusible at a white heat, *impure silica* may fuse, or at least 'frit,' even at lower temperatures. Silica is easily recognised by the following

Blowpipe tests.—When heated (on a platinum wire) with *carbonate of soda*, it readily fuses together with the soda *with evolution of carbonic acid* and formation of a bead, which, if a sufficiency of silica is present, remains clear and transparent on cooling. Silicates rich in silica behave like pure silica. When fused with *microcosmic salt* (*i.e.* with metaphosphate of soda) it remains *undissolved.* If a *silicate* is heated in a microcosmic salt bead, the bases are dissolved while the silica (if present in sufficient quantity) separates out in the form of a 'skeleton' which retains the form of the original specimen.

442. *Hydrates of Silica.*

The dioxide SiO_2 does not combine directly with water, but hydrated silica exists ready formed in nature. The so-called '*Infusorien-Erde*,' for instance, of which large deposits are found in the Lüneburger Heide in Hanover, consists substantially of powdery amorphous hydrated or partially hydrated silica. Besides, hydrated silica can be produced artificially in various ways; for instance, by the decomposition of *chloride of silicon* or of *fluoride of silicon* by water; from numerous *silicates* by decomposing them with hydrochloric or sulphuric *acid.* In all these reactions the silica is separated out in the form of gelatinous precipitates or of coherent jellies—from certain silicates it is obtained in the form of a powder—consisting of highly unstable hydrates of rather indefinite composition. All these hydrates readily give up part of their water on mere exposure to the air, and the rest at temperatures far below dull redness. Precipitated hydrated silica ('silicic acid') in all its forms is almost insoluble in water and in dilute acids, and yet, in the decomposition of a silicate by aqueous acids, a part of the liberated silica always remains dissolved—as '*colloidal silica*' (n($SiO_2.xH_2O$)—where n is probably a very large number). When a solution of alkaline silicate is poured into an *excess* of dilute hydrochloric acid, the whole of the silica remains dissolved in the colloidal state, and when the mixture is subjected to *dialysis*, *i.e.* made to communicate with a mass of pure water through a membrane of vegetable parchment (or of other 'colloidal' matter), the chlorides gradually pass out into the water, and there is ultimately obtained a pure aqueous solution of colloidal silica, which can be boiled down undecomposed in a flask till it acquires a strength of about 14 per cent. of SiO_2. When such a solution is mixed with even small quantities of certain substances, *e.g.* carbonate of soda, it at once solidifies into a jelly. When a solution of colloidal silica (in water or hydrochloric acid, etc.) is evaporated to dryness and dehydrated as far as possible at 100°–105°, the silica is rendered *absolutely insoluble* in water and acids.

443. *Solubility Relations of Silica and its Hydrates.*

Gelatinous hydrated silica is nearly, and anhydrous silica —in all its forms—absolutely, insoluble in water and in ordinary dilute acids. A boiling solution (saturated in the cold) of *carbonate* of soda, dissolves all kinds of precipitated silica, even if it has been previously dehydrated at or below a red heat; in the latter case, however, the solution takes the longer the more strongly the precipitate had been heated. The solution, when diluted and allowed to cool, deposits almost the whole of its silica as a gelatinous precipitate. *Native silica* of any of the three classes named under (1.), (2.), (3.), on page 260 is not appreciably attacked by this solvent. *Caustic potash ley* in the *heat* readily dissolves all kinds of artificial silica, and also—

though somewhat less readily—finely powdered native amorphous silica. The native crystalline modifications are not much attacked. *All kinds of silica*, if in a sufficiently fine state of division, are easily dissolved by aqueous *hydrofluoric acid* with formation of a solution of *hydrofluosilicic acid*, which, on evaporation to dryness in a *platinum* basin, leaves *no* residue.

444. *Silicates*,

of all classes of salts, are the ones of which nature supplies to us both the greatest variety and the greatest abundance. The greater part of the known portion of the earth's crust consists of silicates. Besides these minerals there are a great many silicates which have been produced by dry-way operations. Silicates resulting from wet-way processes have as yet been little investigated. Silicates, both in regard to the combinations of bases which may be associated together in one species, and in regard to the proportions in which these bases and the SiO_2 may be combined with one another, exhibit such an immense diversity of composition, that chemists, to formulate these compositions, have had to invent a whole series of fictitious silicic acids: $nSi(OH)_4-mH_2O$, where $n = 1, 2, 3, \ldots$ and $m = 0, 1, 2, \ldots$ and $2m < 4n$, and besides, to assume that any two isomorphous silicates of analogous atomic constitution may crystallize together in an infinite variety of proportions into homogeneous molecular mixtures. This, in regard to the majority of native silicates, comes very nearly to the same as saying that these minerals are compounds $a\mathrm{SiO_2} + b(\mathrm{Al, Fe})_2\mathrm{O_3} + c(\mathrm{Mg, Ca, K_2, Na_2, H_2})\mathrm{O} + d\mathrm{Aq}$, where a, b, c . . ., supposing even the formula to be on its lowest terms, may assume a great number of different values, and any, except a, may be $= 0$. The law of limitation is not known. But it may be stated that in the vast majority of native silicates, the ratio $2a : (3b+c)$ has been found to be expressible with sufficient exactitude by means of integers less than [illegible].

445. Alkaline silicates.—Ammonia dissolves freshly precipitated silica, but there is no definite silicate of ammonia known. Numerous silicates of *potash* or *soda* (simple and double) can be produced by fusing silica together with caustic or carbonate of alkali—as glassy masses which are the more readily soluble in water the greater the proportion of base they contain. Exs.: $K_2O.SiO_2$—deliquescent, easily soluble. $K_2O.4SiO_2$ ('*water-glass*') not readily soluble in cold, but largely (though slowly) dissolved by boiling water. Alkaline silicates can be fused together with silicates of other metals. All ordinary kinds of **Glass** are alloys of such compounds. **Examples.**—'*German glass*' is an alloy of alkaline silicates with silicates of lime and alumina. It is the harder, the less fusible, and the less acted upon by water and acids, the greater the relative quantity of Al_2O_3 or CaO it contains. In the softer varieties (which serve for the manufacture of ordinary chemical glass apparatus') the alkali consists almost entirely of soda. The '*hard Bohemian glass*,' which combustion-tubes are made of, is a potash glass of the approximate composition $2(K_2O.3SiO_2)+3(CaO.3SiO_2)$. This kind of glass is not only much harder and more difficultly fusible, but also far less attacked by water and acids than soft German glass. *English flint-glass* is a lead-potash glass, the composition of which generally approximates to $2(K_2O.2SiO_2)+3(PbO.2SiO_2)$. It is beautifully transparent, and refracts, and disperses light most powerfully; but it is very soft, very easily fusible, and is strongly attacked by water and acids. When heated in a reducing blowpipe flame it becomes black from reduced lead.

446. *Reactions of Solutions of Alkaline Silicates.*

The solutions are *strongly alkaline* to test paper. The dissolved silicate is decomposed by all ordinary *acids*, including carbonic; but of the silica thus liberated only a part separates out (as a gelatinous precipitate), while the rest remains dissolved as colloidal silica. (Comp. § 442.)

Calcium, *barium*, *lead*, *silver* salts precipitate silicates of indefinite composition, which are all readily decomposed by acids. Excess of *sal-ammoniac* (especially in the heat), and also *carbonate of ammonia*, precipitate the silica almost completely.

447. *Analysis of Silicates.*

Silicates, from the stand-point of the analyst, may be classified as follows :—

(1.) Such as are soluble in *water:* alkaline silicates only.

(2.) Silicates which, though insoluble in water, when finely powdered, can be completely disintegrated by means of *hydrochloric acid.* To this category belong the majority of those native silicates which contain chemically combined water, for instance the '*zeolites*' (Natrolite, stilbite, etc.), and most of the slags formed in metallurgical operations. The zeolites, when dehydrated by ignition, are, as a rule, no longer decomposible (practically) by hydrochloric acid. There are, on the other hand, some silicates which are more easily disintegrated after ignition than they are in their natural state (Exx. Garnet, Epidot). Wallastonite, leucite, lapis-lazuli are examples of anhydrous silicates, which, in their natural state, are readily decomposed by hydrochloric acid. To analyse a silicate of this class, it must first of all be reduced to an impalpable powder. A convenient quantity (say one gramme) is then digested in a porcelain basin with hydrochloric acid until the undissolved part consists entirely of soft silica (no longer grits under the stirring-rod). Sometimes the strong, in other cases the dilute, acid works better. The mixture is evaporated to dryness, and dehydrated as far as possible at a temperature of 100°–105° to render the whole of the silica insoluble, and the residue, after cooling, moistened with strong hydrochloric acid, and allowed to stand for about half an hour, to reconvert into normal chlorides any alumina or oxide of iron that may have been formed. The mass is now treated with hot water, when all the silica remains as an insoluble powder, while the metals pass into solution as chlorides.

(2.) *a.* By way of appendix to class (2.) it may be stated that there are a few silicates which, though not completely decomposible by hydrochloric acid, can be easily disintegrated by treatment in the heat with *oil of vitriol*, diluted with about one-third of its weight of water. The kaolins and clays belong to this class.

(3.) **Silicates not decomposible by ordinary acids.**—This class forms the great majority. Keeping aside a very few exceptions, all these silicates (and, of course, *a fortiori*, all those of classes (2.) and (2)*a*, can easily be disintegrated by fusion with alkaline carbonate. Reduce the silicate to an impalpable powder, mix one gramme of it with from 2-4 grms. of dry *carbonate of soda*—with more or less according to the nature of the substance—and heat the mixture in a platinum crucible, first for some time on a simple Bunsen's lamp, and then over a gas blowpipe, until the fused mass no longer froths up from carbonic acid. This point will be reached after about ¼ or ½ hour's heating. If, instead of carbonate of soda (or potash), a mixture of thirteen parts of carbonate of potash and ten parts of carbonate of soda be used—which fuses much more easily than either of its two components does—the disintegration can often be completed over an ordinary Bunsen's lamp. The fused mass is digested with water in a porcelain basin until it is completely softened up, then supersaturated with hydrochloric acid, and the mixture treated as in the case of a silicate decomposible by acids. For practical reasons the filtrate from the silica is unavailable for the detection even of that one of the two alkalies which may not have been introduced with the disintegrating reagent.

Of methods of disintegration *allowing* of an examination for *alkalies*, the best is to decompose the silicate with *hydro-*

fluoric acid, and the most convenient form in which this reagent can be applied is that of **fluoride of ammonium.** Mix one gramme of the very finely powdered silicate with 3 to 4 grms. of the solid fluoride in a platinum basin, moisten the mixture with dilute sulphuric acid (which must be sufficient, but not immoderately more than is required to convert the bases into sulphates), and next heat on a water-bath as long as visible vapours (SiF_4, etc.) are going off. Then gradually raise the heat—always stirring up with a platinum spatula—until the whole of the fluorine and the excess of sulphuric acid are expelled.* The residue is free from silicon, and contains the bases as sulphates, which, as a rule (*i.e.* in absence of $BaSO_4$ and $PbSO_4$), are all readily soluble in water acidified by hydrochloric acid. *Many* silicates can be completely decomposed by means of **baryta,** *i.e.* $Ba(OH)_2$. Mix one gramme of the finely powdered silicate intimately with four grammes of the reagent, and expose the mixture in a platinum crucible for half an hour to the highest temperature producible by means of a Bunsen's lamp. The ignited mass—which is sometimes fused, sometimes only 'sintered'—is decomposible by aqueous hydrochloric acid. The rest requires no explanation.

According to *Lawrence Smith* all native silicates can be completely decomposed by means of the following process: —Mix 0·5 gramme of finely powdered silicate with 4 grms. of precipitated granular **carbonate of lime**† and 0·5 grms. of sal-ammoniac, and heat the mixture in a platinum crucible, first gently from above downwards, until the sal-ammoniac is all converted into chloride of calcium, then for a time on a Bunsen's lamp, and at last for half an hour over a gas-blowpipe. The sintered mass when digested with water until the excess of lime is completely slacked, and then filtered in the heat, yields a liquid free from silica, and containing the whole of the alkali-metals as chlorides.

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* This operation, on account of the poisonous nature of the hydrofluoric acid vapours, must be conducted in a good draught-place, and it is just as well also to protect the hand which governs the spatula by rubbing it with grease, and then covering it with a glove.

† Prepared by precipitating a dilute solution of chloride of calcium, at 70°, with excess of carbonate of ammonia, and washing the precipitate with hot water.

448. *The 'Silica' obtained in a Silicate analysis*

is not unfrequently contaminated with alumina, oxide of iron, or undecomposed silicate, and occasionally is found to contain traces of certain rare foreign acids, *e.g.* titanic; in exact analyses therefore, it should never be taken for what it is supposed to be before its purity has been proved. The best test is to subject it to the fluoride of ammonium process just described for silicates. *Pure* SiO_2 will of course leave no residue; foreign oxides (including TiO_2) remain as such, or as sulphates.

449. **Hydride of Silicon** (SiF_4?).—Known only as an admixture of the hydrogen obtained in the decomposition of certain silicides (*e.g.* of magnesium) by dilute hydrochloric acid. Such hydrogen is spontaneously inflammable, and burns with formation of a smoke of silica. The gas when passed through a red-hot tube, deposits amorphous silicon. The flame deposits stains of the same substance on a porcelain plate held in it. In *nitrate of silver* the gas produces a black precipitate of metallic and silicide of silver.

VII. FLUORINE.

450. *Fluorine*, F, though widely diffused, is little abundant. Of the small number of minerals which are essentially fluorine compounds, the most important are **fluorspar** CaF_2 (found chiefly in Derbyshire), and **cryolite** $AlNaF_6$, of which large and very pure deposits exist in Greenland. Phosphate of lime, in all its native forms, is invariably accompanied by fluoride of calcium. In phosphorites, coprolites, fossil bones, the quantity of this constituent, as a rule,amounts to several per cents.; a fossil bone analysed by *Baumert* contained 17°/₀ of CaF_2. The bones of all vertebrata contain small quantities of fluoride of calcium.* Traces of fluorine are met with in many *silicates*, *e.g.* in the trap rocks of Edinburgh, and in the granite of Aberdeenshire.

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* Heintz found in the inorganic part of a human thigh-bone 3 per cent. of CaF_2. According to Nicles, however, bones contain only about 5 Ctgr. of fluorine per *kilogramme*.

Elementary Fluorine,

as also the oxides and hydroxides of the element, are unknown.

451. *Hydrofluoric Acid* HF,

*forms (at 15°) a colourless mobile liquid of 0·9879 spec. grav. at 12°·8 which boils at 19·°4 but far below this temperature emits copious vapours. It does not freeze even at – 34°·5. It is very hygroscopic; the vapours when in contact with moist air form dense clouds. It is abundantly dissolved by *water*, with evolution of much heat. The behaviour of the aqueous acid on boiling is similar to that of hydrochloric acid; the hydrate which distils unchanged at the ordinary atmospheric pressure has the approximate composition $HF.2H_2O$. The action of hydrofluoric vapours on the respiratory organs is not unlike to, but infinitely more violent and dangerous than, that of hydrochloric acid.
Pure anhydrous fluoride of hydrogen (whether liquid or gaseous) does not act on glass; but if even slightly contaminated with moisture, it corrodes glass (and silicates generally) most powerfully.* The aqueous acid acts similarly to the gas; the first step in the reaction always being $SiO_2+4HF=SiF_4+2H_2O$. Aqueous hydrofluoric acid acts readily on most ordinary metals; lead, silver, platinum, and gold, however, are not attacked. *Titanium* and graphitoidal *silicon* are not attacked by the *pure* aqueous acid, but dissolved by a mixture of it with *nitric* acid. Gold and platinum are not affected even by nitro-hydrofluoric acid.

452. Metallic Fluorides.—Aqueous hydrofluoric acid has all the properties of a strong acid. With *ammonia*, *potash*, *soda*, it forms two series of salts; viz., normal fluorides RF, and acid fluorides RHF_2. They all form anhydrous crystals. The fixed alkali salts RHF_2 when heated break up into RF and HF gas. The two sodium salts are sparingly soluble in water (the salt NaF dissolves *slowly* in twenty-five parts of cold water, and is not much more readily soluble in the heat); the other alkaline salts of the acid are readily soluble in water. The aqueous solutions of all alkaline fluorides attack glass; the acid salts more powerfully than the normal ones. A solution of fluoride of ammonium NH_4F, when evaporated, loses NH_3, and, consequently, when concentrated in glass vessels, corrodes them most powerfully. The salts SnF_2(SnF_4 is not known for itself), SbF_3, AgF, $HgF_2 + 2H_2O$ are crystalline and soluble, most other normal fluorides are sparingly soluble or insoluble in water. AsF_3, Cr_2F_6, are volatile liquids, decomposed by water into the corresponding oxides and HF.—Most heavy-metallic fluorides in presence of water are very prone to give up acid and pass into oxy-fluorides. The fluorides of the *barium group* metals are *not* decomposed by fusion with alkaline carbonates; but they can be decomposed by fusion with a mixture of the same reagent and *silica.*

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* *Gore*, Jahresber, 1869, 225.

Reactions for the detection of Fluorides.

453. (a) *In Solids.*

Metallic fluorides (with very few exceptions) are decomposed by *concentrated sulphuric acid* with evolution of hydrofluoric acid, which is easily identified by its characteristic action on glass. To test a mineral, etc., for fluorine, provide the convex side of a watch-glass with a coating of bees' wax; and by means of a pencil consisting of a material soft enough to be sure not to scratch the glass, make an inscription on the waxed side, so as to lay bare the glass. On the other hand, mix some of the finely powdered substance with oil of vitriol in a platinum crucible, cover the crucible with the watch-glass, and, after having poured some cold water into the latter to keep the wax from melting, leave the whole to itself in a warm place for a sufficient time. Now remove the wax coating, the bulk with the aid of heat and mechanical means, the rest with turpentine or benzole. The inscription will be found engraven in the glass; slight etchings become more distinct when breathed upon. In case of a substance consisting substantially of a fluoride, the gas will produce a visible etching in ¼ hour, or even less; *traces* of fluorine may only reveal themselves after twenty-four hours. In searching for small quantities of fluorine regard must be paid to the fact that the softer kinds of glass are liable to get corroded by *ordinary* acid vapours. Hence a globular flask made out of a combustion-tube is a safer HF-indicator than an ordinary watch-glass. *Nicklès* recommends a plate of *rock-crystal*, which is absolutely proof against any ordinary acids. This test is obviously inapplicable to substances containing enough of *silica* to convert their fluorine into SiF_4. In these the least traces of fluorine may be detected by the following reaction:

When a mixture of a *fluoride and a silicate* is heated with oil of vitriol, gaseous fluoride of silicon is formed, which, when it comes in contact with *water*, is decomposed as follows: $3\,SiF_4 + 2H_2O = SiO_2$ (hydrated) $+ 2\,SiF_4.F_2H_2$ (hydrofluosilicic acid). Mix the finely powdered substance with sand and oil of vitriol in a platinum crucible; heat gently, and hold in the crucible a drop of water suspended at the end of a thick platinum wire. The fluoride of silicon, if present, will soon cause the formation on the water of a pellicle of *silica*. Another *modus operandi* is to place the mixture in a small dry flask, provided with a gas-evolution tube, and after having, if necessary, added a granule of marble to produce a current of gas, to pass the gas into water. If the precipitate of silica is not distinct, neutralize with carbonate of ammonia ($SiF_6H_2 + 3(NH_4)_2O = 6NH_4F + SiO_2 + H_2O$); filter and evaporate the fluoride of ammonium, either in a glass basin, when the fluoride will reveal itself by dimming the glass, or else in a platinum crucible on a water-bath, when dry fluorhydrate $NH_4.H.F_2$ will remain, which can be identified by the test previously given.

454. (b) *In Aqueous solutions.*

From a solution of a fluoride (*e.g.* NaF, KF, etc.)—*Chloride of calcium* precipitates fluoride of calcium CaF_2 as a semi-transparent, gelatinous mass, which becomes distinctly visible only after it has settled. The precipitate, as it is when produced in the cold, cannot be separated out by filtration. After addition of ammonia and heating, filtration becomes practicable, but it is scarcely possible to effectually wash the precipitate. Precipitated fluoride of calcium is somewhat difficultly soluble in hydrochloric and in nitric acid, and from the solutions can, in general, not be reprecipitated by ammonia, as the salt is very appreciably soluble in ammonia-salts. *Chloride of barium* produces a thick voluminous precipitate of fluoride of barium, the solubility-relations of which are the same as those of the calcium salt. *Sulphate of magnesia* gives a voluminous precipitate soluble in a large excess of the precipitant, and soluble also in sal-ammoniac. From either solution the fluoride of magnesium is completely reprecipitated by ammonia. *Nitrate of silver* gives no precipitate. *Acetate* or *nitrate of lead* precipitates, from the aqueous acid as well as from the alkaline salts, voluminous fluoride of lead, soluble in nitric acid and in caustic potash. The precipitate is slightly soluble in water, but the solution (unlike that of $PbCl_2$) gives only a very insignificant precipitate with ammonia.

455. *Fluosilicates.*

Hydrofluosilicic acid $SiF_4.2HF$ (*v.* supra) is known only as an aqueous solution, which does not act much on glass or porcelain *in the cold*, and which acts strongly on litmus, and on basic oxides and hydrates with formation of *fluosilicates*. The aqueous acid, when evaporated in platinum, breaks up into SiF_4+2HF, and hence leaves ultimately *no* residue. Glass and porcelain vessels, when used for the evaporation of the acid in the heat, are strongly corroded.

Fluosilicates.—Only the normal salts SiF_6R_2 (where $R_2=K_2$, Na_2, Ca'', etc.) are known. These are mostly crystalline salts soluble in water. The least soluble are those of the alkali-metals and of barium. (Comp. §§ 220 and 254.) The free acid, when *exactly* neutralized with *ammonia*, is converted into $SiF_4.(NH_4)_2F_2$, an easily soluble crystalline salt; when mixed with *excess* of ammonia, it yields a precipitate of silica and a solution of *fluoride* of ammonium. Similarly the acid (and aqueous solutions of the potash or soda salt which colour blue litmus red) when neutralized *in the heat* with caustic fixed alkali, give precipitates of silica and solutions of alkaline fluoride. Fluosilicates when heated to redness are reduced to fluorides with evolution of fluoride of silicon. When heated with *concentrated sulphuric acid*, they give off fluoride of silicon and hydrofluoric acid, and ultimately leave residues of sulphates. When a fluosilicate solution is mixed with dilute sulphuric acid, and the mixture concentrated in the heat in a glass vessel, the glass is strongly attacked. By these properties, and by the relative insolubility of the potash and the baryta salt, fluosilicates are easily distinguished from other classes of salts. The barium salt, being very little soluble in dilute hydrochloric acid, is liable to be mistaken for the sulphate, from which however it can be distinguished by its possessing the properties of fluosilicates just enumerated, and by its not giving a hepar when heated with carbonate of soda on charcoal in the reducing flame.

Note.—The fluosilicates are only one branch of a large family of double fluorides, all constituted according to the general formula $X^{iv}F_4.2RF$, where X^{iv}=Si, Sn, Ti, or Zr, and of which those containing the same basilous metal (R) are in general isomorphous with one another. Each class, of course, exhibits its own specific reactions.

456. Fluoride of Boron BoF_3—formed by the action of hydrofluoric acid on the oxide Bo_2O_3—is a colourless gas which is abundantly, dissolved by water, with formation of a variety of '*fluoboric acids.*' The acid $BF_3.HF$ is known only as an aqueous solution, which in its general character is not unlike aqueous fluosilicic acid. Its salts

BoF_4R are mostly soluble in water. On ignition they split up into fluorides FR and BoF_3. With oil of vitriol they yield BoF_3 and HF. The potash and soda salts are *not* decomposed by even boiling caustic alkali, which distinguishes them from the fluosilicates.

VIII. CARBON.

Of the immense number of carbon compounds, only a small selection can be noticed here individually. It is however hardly necessary to say that what will be given under general headings such as 'elementary analysis of carbon compounds' is not by any means confined in its applicability to the substances previously considered.

457. *The 'Free Element'*

exists as *diamond*, *graphite*, and in a variety of other forms known as '*charcoal*.' All these **carbides of carbon** are solids, which, even at the strongest heat of any furnace, prove absolutely infusible and non-volatile. They are insoluble in water or any other menstruum, and insoluble also—as carbon—in any acid. They are not acted on, at any temperature producible by ordinary heating-appliances, by free *nitrogen*, *chlorine*, or *hydrogen*. When heated in *oxygen*, they burn into *carbonic 'acid'* CO_2; but they do not all of them burn with the same degree of facility. Graphite and certain dense kinds of charcoal, when heated even in oxygen, burn only very slowly.

Diamond is a rare mineral, occurring generally in isolated octahedra or other forms of the regular system, the faces being frequently curved. The colour varies from absolute colourlessness to jet-black; but it always possesses the same characteristically high refractive and dispersive power for light. It is the hardest of known solids. Spec. grav. 3·5 to 3·6.

Graphite occurs in nature as a mineral, which sometimes presents itself in hexagonal crystals, but far more frequently forms dense amorphous, or scaly, opaque masses, exhibiting a black colour and a semi-metallic lustre. Graphite is very soft, and easily reduced to a black slippery powder. Spec. grav. = 1·2 (about). Native graphite is generally contaminated with more or less of incombustible matter, but the combustible part always consists of carbon only.—Grey cast-iron is an intimate mixture of carbide of iron and small crystalline particles of *graphite.*

Charcoal.—A generic term applied to the variety of carbides of carbon contained in those black substances which, in the decomposition of organic compounds at high temperatures, in absence of air, are obtained as final products. Regarding the properties of the several kinds of charcoal, we must refer to hand-books of descriptive chemistry; suffice it to state that all 'charcoals,' even if produced at the highest temperatures, contain hydrogen—and those derived from nitrogenous matter also nitrogen—in chemical combination with the carbon. The hydrogen can be removed by strong ignition in chlorine.

458. *Carbonic Acid.*

The anhydride CO_2 is a colourless gas of 1·524 spec. grav. (Air = 1), devoid of smell, but possessing a faint sourish taste. Coefficient of absorption at 15°; for water = 1·00, for alcohol = 3·20. The aqueous solution slightly reddens litmus; the dissolved gas is easily expelled on boiling. The gas is readily absorbed by solutions of potash, soda, baryta, or lime; by the latter two solutions with formation of a white precipitate (of $BaCO_3$ or $CaCO_3$). It is not changed by acid chromate or permanganate, which distinguishes it from SO_2.

The acid CO_3H_2 does not exist.

Metallic carbonates.—The normal carbonates R_2CO_3 of the *alkalies* and of *baryta* are perfectly stable at a red heat; those of strontia and lime, at these temperatures, are decomposed, the former very slowly, the latter more readily, into CO_2+RO; while in the case of magnesia and heavy-metallic carbonates lower degrees of heat suffice to effect a similar decomposition. The carbonates R_2CO_3 and $RHCO_3$ of the alkalies are more or less readily soluble, the rest are mostly insoluble in water; many dissolve more largely in carbonic acid solution than in pure water.

Detection of combined CO_2.—All metallic carbonates (except one or two refractory native ones) are readily decomposed by dilute mineral acids, with evolution of carbonic-acid gas, which is easily recognised by means of *lime-water*, or—what is better—*baryta-water* (*vide* supra). If the gas evolution is too slight to constitute a current, add a piece of *zinc*, and so sweep out the CO_2 by means of hydrogen. The refractory native carbonates referred to must be decomposed by ignition with *borax*-glass or *bichromate of potash*, or *silica*.

459. *Carbonic Oxide* CO

is a colourless, inodorous poisonous gas, barely soluble in water, not absorbed by alkalies or acids, but readily absorbed by a solution of *cuprous chloride* in hydrochloric acid or ammonia. It is readily inflammable, and burns with a blue flame into carbonic acid.

460. *Bisulphide of Carbon* CS_2,

producible by the action of sulphur-vapour on charcoal at a red heat, forms a colourless liquid of 1·271 spec. grav., possessing a characteristic smell, and boiling at 46°·2 (under 760 mm.) It refracts and disperses light strongly. It is insoluble in water, but miscible with alcohol, ether, and liquid hydrocarbons. It is a solvent for iodine, phosphorus, sulphur, and many solid hydrocarbons, *e.g.* for gutta-percha, and for many fats, oils, and resins. It is very inflammable, and burns into CO_2+2SO_2. It dissolves in aqueous solutions of *potash* (as $2K_2CS_3+K_2CO_3$); the solution when boiled with *acetate of lead* gives a black precipitate. CS_2 unites directly with *triethyl-phosphine* into red crystalline laminæ $PEt_3.CS_2$ crystallizable from alcohol. By these two reactions even traces of bisulphide-of-carbon vapour diffused through coal-gas (or other diluents) are readily detected.

461. *Carburetted Hydrogens.*

Regarding this very numerous class of compounds we must refer to the hand-books of organic chemistry.

462. *Carbides of Metals.*

Many metals when fused together with carbon, or when formed by reduction of their oxides with carbon, unite with more or less of that element into what, from the stand-point of the analyst, may be called *alloys* of the respective metals with carbon. Cast-iron and steel are examples of such alloys. When metallic carbides are disintegrated by means of acids, part of the carbon, in general, separates out, while the rest is either oxidized, or, in the case of non-oxidizing acids, evolved in the form of carburetted hydrogens. All carbides, when burnt in oxygen or with chromate of lead, give up their carbon as carbonic acid.

Cyanogen (NC) – or 'Cy.'

463. Dicyanogen $(NC)_2$: a colourless gas of the spec. grav. 1·806 (Air = 1), possessing a pungent odour, not unlike that of prussic acid. It can be condensed into a liquid, which, under 760 mm. pressure, boils at -21°. Cyanogen is inflammable and burns with a purplish flame into carbonic acid and nitrogen. It is soluble in $\frac{2}{9}$th of its volume of water; the solution soon undergoes spontaneous decomposition into a variety of products. It is absorbed by caustic potash ley with formation of cyanide and cyanate.

464. Cyanhydric acid NCH (*not* producible synthetically from $(NC)_2$ and H_2) is a colourless very volatile liquid of spec. grav. 0·697 at 18°, boiling at 26°·5, soluble in all proportions in water *without* formation of hydrates. Even dilute solutions readily give up their NCH to air, and hence smell strongly of HNC. Both the substance NCH and its aqueous solution, when left to themselves, undergo spontaneous decompositions of a very complex character; the aqueous acid yields formate of ammonia amongst other products. The presence, in the aqueous acid, of small quantities of any strong mineral acid considerably retards its decomposition. Aqueous *cyanhydric acid* acts but slightly on litmus paper, and only very sluggishly reacts with solutions of even strong bases such as potash or baryta. It dissolves red oxide of mercury with formation of a solution of mercuric cyanide $(NC)_2Hg$, which in this form presents great stability. From an aqueous solution or mixture containing *free* hydrocyanic acid, this constituent can be eliminated by distillation; the NCH passes over with the first fractions of the distillate. Should the distillate contain hydrochloric or other (stronger) acids, these can be removed by re-distillation with excess of *borax*, which renders them non-volatile without acting on the hydrocyanic acid. Having once obtained the HNC as a sufficiently pure aqueous solution, we can identify it by the following tests.

465. *Reactions of Aqueous Hydrocyanic Acid.*

(1.) *Nitrate of Silver* precipitates cyanide of silver AgNC, which is very similar in appearance to chloride, and, like it, is insoluble in cold dilute nitric (and other mineral) acids, and soluble in ammonia, but can be distinguished from chloride: (*a*) as by its being decomposed, on boiling, by *hydrochloric*, and also, though less easily, by dilute *sulphuric* acid with evolution of NCH; (*b*) by its comportment at a *red heat.* Cyanide of silver when heated melts, and is then decomposed into cyanogen and a mixture of metallic, and paracyanide of, silver, which latter then, on continued heating in air, passes, first into a mixture of metal and carbide, and ultimately into pure metal.

(2.) *Ferroso-ferric salt.*—When aqueous hydrocyanic acid is mixed successively with (1) excess of caustic soda, (2) *partially* oxidized ferrous sulphate or chloride, (3) excess of hydrochloric acid, there is formed a *blue* precipitate or (in the case of a trace of HNC) a green suspension of '*Prussian blue.*'—$6KNC + FeCl_2 = 2KCl + (NC)_6FeK_4$.—$(NC)_6FeK_4 + 4fe^*Cl = 4KCl + (NC)_6Fe.fe_4$ (Prussian blue).

(3.) *Polysulphide of ammonium* $(NH_4)_2S.S_x$, when added to aqueous hydrocyanic acid, produces sulphocyanate of ammonium, which, after removal of the excess of reagent by evaporation at a *gentle* heat, can be recognised by the characteristic intense blood-red colour which it gives on addition of ferric chloride.

The three tests are all very delicate; (2) and (3) are besides highly characteristic.

Metallic Cyanides

may be classified as follows:—

466. (a) *Cyanides of the alkali- and alkaline-earth metals*, NCR', where $R' = K, Na, \frac{1}{2}(Ba, Sr, Ca)$. These are white solids, which, when heated for *themselves*, *i.e.* in an inert atmosphere such as nitrogen, prove perfectly stable even at very high temperatures; the alkaline ones however at a bright red heat are volatilized. When heated in *steam*, they are decomposed with formation of *ammonia* and carbonates. When heated in air they undergo partial oxidation, the cyanides of potassium and sodium when fused with certain metallic oxides (*e.g.* PbO, SnO_2, Fe,O_3) are completely oxidized, into *cyanates* $R'(NC)O$, the metallic oxides being reduced to metals. When heated with sulphur or certain metallic sulphides they are transformed into *sulphocyanates* $R(NC)S$.

They are all soluble in water with formation of strongly alkaline solutions, which are readily decomposed by *acids* with elimination of hydrocyanic acid. Even carbonic acid, when passed through the solutions, effects a very far-going decomposition. The three tests given in § 465 for hydrocyanic acid apply also to solutions of the class of cyanides under consideration, except that in the case of alkaline cyanides at least, *nitrate of silver* gives a *permanent* precipitate only, when more than 1$AgNO_3$ has been added for every 2RNC, lesser quantities of the reagent being converted into soluble double salts RNC+AgNC.

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* $fe = \frac{1}{3}Fe = 18\frac{2}{3}$ parts of ferricum.

In solutions of most heavy-metallic salts (*e.g.* in aqueous chloride or sulphate of iron, nickel, cobalt, zinc) *alkaline cyanides* produce precipitates consisting of, or at least containing, the respective heavy-metallic cyanides. These are all soluble in excess of alkaline cyanide with formation of double cyanides, which in this form exhibit a higher degree of stability than the alkaline cyanide itself, and which are not decomposable by alkaline hydrate or carbonate.

467. (b) *Cyanide of mercury* $Hg(NC)_2$.—Red oxide of mercury readily dissolves in aqueous hydrocyanic acid with formation of a solution of this salt, which, compared with solutions of class (a), exhibits a very high degree of stability. The salt is *not* decomposed by even boiling dilute sulphuric acid, and gives *no* precipitate with nitrate of silver. Hydrochloric acid decomposes it with formation of mercuric chloride and hydrocyanic acid, which latter, however, when an excess of acid and heat be employed, may get decomposed into ammonia and formic acid. *Sulphuretted hydrogen* decomposes the solution completely into mercuric sulphide and *hydrocyanic acid.*

468. (c) *Other heavy-metallic* cyanides.*—Excepting tercyanide of gold ($AuCy_3.3H_2O$), which is soluble, all these cyanides are insoluble in water. By exposure to a red heat they are all decomposed in such a manner that the metal ultimately remains as such or as a carbide. Their comportment with aqueous mineral acids is different; some of them (for instance, the cyanides of zinc and cadmium) are readily decomposed by even cold dilute hydrochloric acid; others are decomposed by this acid only on *boiling* (ex.: AgCy);

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* This term is here meant to include Au, Pt, Ag, Cu, Cd, Bi, Pb, Fe, Ni, *Co, Mn, Zn.*

others again withstand the action of even boiling aqueous acids (cyanides of cobalt, nickel, platinum). Most of these cyanides, when boiled with *oxide of mercury* and water, are decomposed with formation of precipitates of metallic hydrates and of solutions of *mercuric cyanide.* The cyanides of cobalt and of platinum, and aurous cyanide (AuCy), however, *cannot* be thus decomposed.

469. (d) *Double cyanides of heavy metals* (c), *and of potassium or sodium.*—This very numerous class may be divided into two sections :—*the first* comprising those which, when treated with acids, behave pretty much like ordinary double-salts, *i.e.* like mixtures of the two component cyanides. To this class belong the double cyanides of alkali-metals, and respectively silver, lead, zinc, nickel. From the solutions of *these* double-salts, the heavy metals can be precipitated, as a rule, by sulphuretted hydrogen or sulphide of ammonium. The *second* section includes those which, although they behave like alkaline salts, do not exhibit any of the ordinary reactions of the ordinary salts (chlorides, etc.) of the respective heavy metals. They behave in fact as if the whole of the cyanogen and the heavy metal formed *one* relatively indivisible radicle. When added to solutions of heavy-metallic chlorides, sulphates, etc., they generally produce precipitates in which the whole or part of the alkali-metal of the original cyanide is replaced by the newly introduced heavy metal. When treated with *hydrochloric*, or dilute sulphuric, acid in the cold, they are more or less completely decomposed with formation of the respective metallo-hydrocyanic acids. When the mixture is boiled, the acid in most cases undergoes decomposition with elimination of part of the cyanogen as hydrocyanic acid—this is the case, for instance, with ferro-hydrocyanic acid ;* but there are a few, of which cobalti-hydrocyanic acid may be cited as an example, the solutions of which prove perfectly stable even on continued boiling. All the double cyanides (d), when heated to redness in absence of water and air, are decomposed with formation of alkaline cyanide and heavy-metallic carbide.

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* Action of dilute acids on ferrocyanade of potassium : (1) $2Cy_6FeK_4+4H_2SO_4=4K_2SO_4+2Cy_6FeH_4$. (2) $2Cy_6FeH_4+2K_2SO_4=Cy_6Fe_2K_2$(white precipitate)+$6HCy+2KHSO_4$.

Analysis of Metallic Cyanides.

470. I. Detection of the Cyanogen.—*All cyanogen compounds*, when ignited in a combustion-tube with excess of *soda-lime*, give up the whole of their nitrogen as *ammonia*. This test, supposing it to give a positive result, proves only the *possible* presence of cyanogen. To see if cyanogen is actually present, (1) distil the substance with *hydrochloric acid* and search for hydrocyanic acid in the distillate; in the case of a negative result, (2) boil another portion with water and *oxide of mercury*, filter off the metallic oxide (and excess of HgO), from the filtrate eliminate the mercury by means of sulphuretted hydrogen, and search in the filtrate for hydrocyanic acid. If this operation also leads to a negative result, cyanogen can be present only as cobalti-cyanide, platino-cyanide (or perhaps in a few other rare states of combination). In this class of cyanides, the presence of the radicle NC *cannot* be demonstrated directly by any analytical methods; but many of the substances belonging to it may be recognised by their own specific properties and reactions.

471. II. Detection of the Metals.—In many cyanides the metals present can be detected by means of the ordinary reagents. But as there are a vast number of cyanides which exhibit anomalous metal-reactions, the only safe process of exhaustive analysis is, to begin by eliminating the cyanogen in such a manner that the metals are obtained as chlorides, sulphates, or in other forms admitting of the direct application of the routine-methods of metal-detection. This, in many cases, may be effected by treatment of the substance with dilute acids in the heat, or with the help of oxide of mercury (*vide* supra), but the only general and throughgoing method is, to *destroy* the cyanogen by treating the substance with *oil of vitriol* in the heat as long as gaseous products are evolved. By this operation, the cyanogen is converted into carbonic oxide and ammonia, while the metals are obtained as sulphates.

472. *Separation of Cyanogen from the Halogens.*

Cyanide and most of the metallo-cyanides of silver being insoluble in water and in dilute mineral acids, a precipitate obtained from a solution of salts by addition of nitrate of silver and nitric acid, is liable to contain the respective cyanogen-radicles besides halogens (Cl, Br, I), the oxyhalogens (BrO_3, IO_3), and sulphur.

To separate haloid (Ag(Cl, Br, I)) from cyanide of silver, we need only boil the precipitate in a retort with dilute sulphuric acid, when the cyanide is decomposed into hydrocyanic acid, which distils over, and sulphate of silver, which can easily be dissolved out from the haloids by means of hot water. Metallo-cyanides—if given as admixtures with haloid of silver—could probably all, like the simple cyanide AgCy, be decomposed by digestion with a solution of alkaline chloride into chloride of silver and solutions of alkaline metallo-cyanides, which latter might then be identified by their specific reactions. To test a precipitate, known to contain cyanide or metallo-cyanide of silver, for admixture of haloid, all that is required is to subject it to a prolonged ignition, whereby all the cyanogen-compounds are reduced to the state of metal (or metallic carbide), while the haloids remain undecomposed. By fusion with alkaline carbonate, these may be converted into sodium salts, which can be extracted by means of water and examined in the usual way.

473. *Appendix to Cyanogen.*

Cyanates.—Alkaline cyanates R'NCO are formed gradually by the action of air, and very readily by the action of many metallic oxides, on the respective alkaline cyanides at a red heat. (Ex. : $NCK+PbO=NCKO+Pb$). Alkaline cyanates, if perfectly dry, stand a red heat without decomposition ; they are soluble in alcohol and in water. The aqueous solutions when boiled are decomposed with formation of alkaline carbonate and of ammonia, thus: $KNCO+2H_2O=NH_3+CO_3KH$. When their solutions are mixed with dilute mineral acid, cyanic acid NCHO is liberated, the greater part of which is at once decomposed into carbonic acid and ammonia; but a small portion of undecomposed acid always escapes with the carbonic anhydride, and imparts to it a characteristic penetrating smell. When their solutions are mixed with sulphate of ammonium, the momentarily formed cyanate of ammonium quickly passes into the state of urea, $NC.(NH_4)O=CO(NH_2)_2$. The cyanates of silver, lead, mercurosum, cupricum are insoluble in water.

Sulpho-cyanates.—Alkaline sulpho-cyanates are obtained by fusion of the cyanides with sulphur or certain metallic sulphides. Ex.: $PbS+KNC=Pb+KNCS$. They are readily soluble in water ; the solutions give white precipitates with those of *cuprous salts* (or cupric ones and sulphurous acid), with *mercurous nitrate.* and with *argentic nitrate.* The silver salt AgNCS is almost as insoluble as the chloride in dilute nitric acid. *Ferric chloride* produces a characteristic intense blood-red colour, which does not disappear on addition of moderate quantities of mineral acid.

Nitroprussides.—The potassium salt is produced in the action of nitrous acid on a cold acidified solution of ferricyanide of potassium, $2Cy_6FeK_2H+2NO_2H=2H_2O+(NC)_2+2FeCy_5(NO)K_2$. The alkaline salts form garnet-red crystals, easily soluble in water. The solutions give precipitates with most heavy-metallic salts. When they are mixed with solutions of *alkaline sulphides,* a very intense (but transient) violet colour is produced. Sulphuretted *hydrogen* does not give the colour. By the action of excess of *caustic alkali,* all nitroprussides are readily decomposed with formation of ferrocyanide.

Fatty Acids.

General Formula, $C_nH_{2n}O_2$.
Potash salts, $C_nH_{2n-1}KO_2$.

474. These acids are all monobasic. Those containing more than three atoms of carbon per molecule exist in a number of isomeric modifications. Examples :—

Name.	Formula.	Melting Point.	Boiling Point.
Formic, . . .	CH_2O_2 . .	1°	100°
Acetic, . . .	$C_2H_4O_2$.	16°·7	119°
Propionic, . .	$C_3H_6O_2$.	?	139°
Ord. Butyric, .	$C_4H_8O_2$.	below − 20°	162°
Valerianic, . .	$C_5H_{10}O_2$.	?	174°*
. . . .	. . . . .	. . . . .	. . . .
Palmitic, . .	$C_{16}H_{32}O_2$.	62°	. . . .
Stearic, . . .	$C_{18}H_{36}O_2$.	69°	. . . .

These acids form at ordinary temperatures colourless liquids or crystalline solids. Those containing from 10 atoms of carbon downwards can be distilled for themselves without decomposition, the higher ones cannot. The C_1, C_2, C_3, and C_4-acids are miscible in all proportions with water; the two latter can be separated out of their solutions by means of chloride of calcium. Valerianic acid dissolves in about 30 times its weight of water; the higher ones are still less soluble. They are all soluble in alcohol. The salts of this series are all readily decomposed by hydrochloric or dilute sulphuric acid with elimination of the respective acids. The potassium and sodium salts are all soluble in water; those of palmitic, stearic, and some of the other acids rich in carbon, are '*soaps*,' *i.e.* their aqueous solutions froth strongly on shaking, and when diluted with much water, are decomposed into a difficultly soluble acid and a more soluble basic salt. The barium and lead salts are generally the less soluble in water the higher they stand in the series.

Only the first acid of the series, formic acid, can be identified, with perfect certainty, by purely qualitative tests; the method to be followed in case of any of the higher ones is to convert it into a definite salt and to identify the salt by its physical properties, solubility-relations, and elementary composition.

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* *i.e.* acid from inactive amyl alcohol.

475. Formic Acid CH_2O_2 forms a colourless liquid of 1·22 spec. gravity, possessing a pungent smell not unlike that of a mixture of sulphurous and acetic acids. It produces blisters on the skin. The aqueous solution is not corrosive, but possesses all the properties of a strong aqueous acid. All formates are soluble in water. The most characteristic salts are: the magnesium salt $(CHO_2)_2Mg$, a crystalline crust soluble in 13 parts of cold water; the lead salt, $(CHO_2)_2Pb$, small transparent crystals soluble in 36–40 parts of cold water; formate of mercurosum soluble in 520 parts of cold water, the solution is decomposed on boiling with formation of metallic mercury and carbonic and formic acids. The silver salt, while on the whole similar to the mercurosum one, is still less stable. Metallic formates are readily decomposed on ignition without elimination of carbon. The residue consists of carbonate, or of that into which the carbonate would have got converted had it been produced first. When treated with *oil of vitriol* they give off pure carbonic oxide, $CH_2O_2 - H_2O = CO$. When a solution of a formate is mixed with *nitrate of silver*, there may be a crystalline precipitate of formate of silver, but in all cases the mixture, when heated to boiling, deposits black metallic silver with evolution of carbonic acid. The same reduction takes place if free formed acid is used; but it fails in presence of excess of ammonia. When a solution of formic acid is boiled with red *oxide of mercury*, the acid is gradually, and at last completely, oxidized into carbonic acid and water. A solution of formic acid or of a formate when heated with one of *mercuric chloride* to about 70°–80°, produces a precipitate of *calomel*. The presence of free hydrochloric acid or of large quantities of alkaline chlorides prevents this reduction. Formic acid when heated with a mixed solution of *bichromate of potash* and sulphuric acid, is readily oxidized into carbonic acid.

476. Acetic acid $C_2H_4O_2$ exists in the form of a crystalline solid which fuses at 16°·7, but when once fused may remain fluid at temperatures far below its freezing point. Its smell is less pungent than that of formic. It produces blisters on the skin. The aqueous acid has an agreeable sour taste and smell; its action on litmus and on bases is far less energetic than that of formic acid. Common vinegar is a more or less impure aqueous acetic acid, containing from two to six per cent. of real acid. Most normal **Metallic Acetates** are easily soluble in water. They are all decomposed at a red heat—some of them with elimination of charcoal; the residues otherwise are identical with the ones obtained from the corresponding carbonates. The *potassium* salt is deliquescent; it dissolves in one-half part of water and in three parts of absolute alcohol. It unites with acetic acid into a characteristic crystalline binacetate $C_2H_3KO_2.C_2H_4O_2.3H_2O$, which, when gradually heated, first gives up its water and then, at 200°, the extra-molecule of acid. The *sodium* salt forms crystals $C_2H_3NaO_2.3H_2O$ soluble in about three parts of cold water. Both alkaline acetates, when heated, are easily dehydrated, and then melt into oily liquids which stand a temperature of 300° without decomposition; all other acetates are decomposed at lower temperatures. Acetic acid is *not* appreciably decomposed when heated with *oil of vitriol.* It *cannot* be oxidized by aqueous chromic acid. Solutions of normal acetates, when mixed with *ferric chloride*, become deep red from formation of ferric acetate, which (unlike the sulphocyanate) is easily decolorized by hydrochloric acid. *Mercurous nitrate*, in not too dilute solutions, produces crystalline precipitates of mercurous acetate easily soluble in excess of precipitant. *Nitrate of silver*, under the same circumstances, produces a crystalline precipitate which can be re-crystallized from hot water without appreciable decomposition. *Mercuric chloride* is *not* reduced by acetates, not even on heating. Aqueous acetic acid when digested with excess of *oxide* of *lead*, yields a solution of basic acetate which colours turmeric paper brown. So far acetic agrees with formic acid; but while the solution of the formate deposits crystals on cooling, the acetate solution refuses to do so.

477. *From a mixed solution of the more volatile Fatty Acids*

the *formic acid* is easily eliminated by prolonged boiling—an inverted condenser being used—with excess of mercuric oxide. (*Vide* supra.) To separate *acetic acid* from its higher homologues, add enough of caustic potash to convert the acetic acid into binacetate, and distil; if a sufficiency of potash was taken, the distillate is free from acetic acid. If a mixture of two of the higher homologues (for instance of the C_3 and C_5 acid) is partially saturated with potash and distilled, the lower (*i.e.* the more volatile) acid predominates in the distillate while the higher (less volatile) one accumulates in the residue.—(*Liebig.*) By the repeated application of this process of partial saturation and distillation, it is possible sometimes, from a mixture of fatty acids, to extract one or the other of the predominating constituents in a state of approximate purity.

478. *Detection of Metals given as Salts of Fatty Acids.*

The presence in a solution of metallic salts of such fatty acids as are, for themselves, soluble in water, does not interfere much with the application of the ordinary methods for the detection of metallic bases as given in Part II. It needs only be observed that a precipitate obtained in the acid liquid by sulphuretted hydrogen is liable to contain *zinc*, *cobalt*, and *nickel*, besides metals of the copper and arsenic groups. If the substance under examination contains higher fatty acids, these must, previous to the application of metal-precipitants, be separated out by means of an appropriate mineral acid and removed: solid or semi-solid ones by filtration, liquid ones by means of a pipette or by distillation.

Acids of the Lactic Series.

(Homologues of Carbonic Acid.)

General empirical formula, $CH_2O_3 + nCH_2$.

„ rational „ $C_nH_{2n}\left\{\begin{matrix}COOH\\OH\end{matrix}\right.$.

The series comprises: Glycollic (oxy-acetic), n=1; Lactic (oxy-propionic), n=2; Butylactic (oxy-butyric), n=3;... Leucic (oxy-capronic), n=5. These acids are diatomic but monobasic. With exception of glycollic, each acid exists in a number of isomeric modifications. We confine ourselves to the consideration of that particular

479. **Lactic Acid** $(CH_3)-(CH)\begin{matrix}COOH\\OH\end{matrix}$, which is contained in sour milk, and obtained by the fermentation of sugar as induced by cheese in presence of chalk or other substances preventing the accumulation of free acid. This acid forms a colourless syrup, miscible in all proportions with water and alcohol, and soluble in ether. When the aqueous solution is shaken with ether, the greater part of the acid passes into the ethereal layer and can thus be extracted. The acid when carefully exposed to higher and higher temperatures, passes first into dilactic acid $C_6H_{10}O_5$, a pale-yellow amorphous bitter mass, and then (at about 210°) into the real anhydride $C_3H_4O_2$, which when rapidly heated breaks up into aldehyde and carbonic oxide. Lactic acid and lactates when heated with *oil of vitriol* are decomposed with copious evolution of *carbonic oxide.*

Normal **lactates** are all soluble in water. Of these the most characteristic are: (1) the *calcium salt* $C_3H_5Ca_{\frac{1}{2}}O_3.\frac{5}{2}H_2O$, which forms small mammelated crystals, difficultly soluble in cold water, but easily soluble on boiling in both water and alcohol; (2) the *zinc salt* $C_3H_5Zn_{\frac{1}{2}}O_3.\frac{3}{2}H_2O$, crusts or large needles soluble in 58 parts of cold and in 6 parts of boiling water. A hot aqueous solution of this salt is completely decomposed by sulphuretted hydrogen.

Note.—An acid isomeric with, and very similar to, lactic acid has been extracted from the juice of flesh. This acid ('sarcolactic') was supposed to be *ethylene-lactic* $\left\{\begin{matrix}CH_2COOH\\ CH_2OH\end{matrix}\right.$ until Wislicenus showed quite lately that it is a mixture of two things; the bulk of it consisting of an ethylidene-derivative '*paralactic acid*,' which forms crystalline zinc and calcium salts, while the rest consists of an acid which refuses to form crystalline salts and probably represents the true ethylene-acid.

Oxalic Acid Series.

General formula, $(COOH)_2+nCH_2$.

Exx.: Oxalic, $n=0$; Malonic, $n=1$; Succinic, $n=2$; Pyrotartaric, $n=3$. Those formulas in which $n>1$, correspond, each of them, to a genus of isomers. These acids are all dibasic. They act on bases much more energetically than the lactic acids do. The free acids are solids soluble in water and in alcohol.

480. Oxalic Acid crystallizes from its aqueous solution in large monoclinometric prisms of the composition $(COOH)_2.2H_2O$, soluble in 8·7 parts of water at 15°, and much more soluble in hot water; soluble in about 4 parts of cold ordinary alcohol. The crystals when kept in a dry atmosphere gradually lose their $2H_2O$; they are readily dehydrated at 100°. The dehydrated acid can be sublimed at 160°–200° with partial decomposition into formic and carbonic acids. The acid, whether free or combined, when heated with *oil of vitriol* is readily decomposed with evolution of the two carbon oxides $(CO+CO_2)$. The *aqueous* acid can be oxidized into *carbonic acid*, by (1) *permanganate of potash* and sulphuric acid; (2) *binoxide of manganese* and sulphuric acid; in both cases with formation of *colourless* manganous salt; (3) *bichromate of potash* and sulphuric acid, with formation of green chromic salt; (4) *chloride of gold*, with precipitation of metallic gold,—and by other oxidizing agents. **Oxalates.**—The alkaline salts are soluble; most other oxalates are insoluble or difficultly so in water, but soluble in hydrochloric acid. All oxalates are decomposed on ignition with elimination of little or no carbon; the metals remain as carbonates or decomposition-products of these. The most characteristic salts are: the acid potash salt $C_2O_4KH.H_2O$, soluble in 40 parts of cold and in 14 parts of boiling water; the sodium salts; $C_2O_4Na_2$ soluble in 31 parts, $C_2O_4HNa.H_2O$ soluble in 60 parts, of cold water; the ammonium salt $C_2O_4(NH_4)_2.H_2O$ soluble in 25 parts of cold water; the lime salt $C_2O_4Ca.H_2O$, regarding whose properties see below. Oxalates are easily recognised—(1) by their comportment on ignition, and on being heated with oil of vitriol (*vide* supra); (2) by the power of their solutions in dilute mineral acids of reducing the oxidizing agents named above with evolution of carbonic acid; and (3) by the following characteristic reaction: solutions of oxalates in water, acetic acid, or ammonia, when mixed with *chloride of calcium*, yield a white, powdery precipitate of oxalate of calcium, which is practically insoluble in water, and in ammonia, and in acetic acid; no other precipitated lime salt exhibits *all* these properties. A solution of free oxalic acid gives a precipitate even with *sulphate*-of-lime solution. In the

481. *Examination of a mixture of Oxalates for Metals*,

we must take care to remember that the oxalates of the barium group are precipitated as such from their acid solutions by ammonia and by sulphide of ammonium, and that chromic oxalate is *not* precipitated by ammonia. Hence the safest course in the analysis of a mixture of metals given as oxalates is to begin by destroying the oxalic acid by ignition or by treatment with oil of vitriol.

482. Succinic Acid $C_2H_4(COOH)_2$ forms white crystals soluble in five parts of cold and in two parts of boiling water, less soluble in alcohol and almost insoluble in ether. When cautiously heated, it first emits irritating vapours, and then, at about 140°, sublimes slowly; when rapidly heated, it melts at about 180° and boils at 235°, being at the same time largely decomposed into water and anhydride. Succinic acid is not attacked by even hot *oil of vitriol;* it also resists the action of all *ordinary liquid oxidants,* for instance that of free chlorine, nitric acid, aqueous chromic acid, and of hydrochloric acid and chlorate of potash. **Succinates** are decomposed on ignition, most of them with formation of charcoal. The (K-, Na-, NH_4-, Mg-, Mn)- salts are readily soluble in water; the barium salt $C_4H_4BaO_4$ and the calcium salt $C_4H_4CaO_4.(H_2O$ or $3H_2O)$ are sparingly soluble in water and in acetic acid, and insoluble in alcohol. The normal lead salt is sparingly soluble in water and in acetic acid, and insoluble in alcohol. The silver salt $C_4H_4Ag_2O_4$ is nearly insoluble in water and in acetic acid. Neutral solutions of alkaline succinates exhibit the following **Reactions**: *chloride of barium,* when used in conjunction with alcohol and ammonia, gives a white precipitate. *Ferric chloride* precipitates the greater part of the acid in the shape of a brownish pale-red salt, which is easily soluble in mineral acids and, by the action of ammonia, is decomposed so that the greater part of the acid is extracted as ammonia salt.

Note.—Pseudosuccinic acid $(CH_3)-(CH)=(COOH)_2$ (carboxyl-propionic) differs from the ordinary acid in many points, for instance in this, that, when heated, instead of giving an anhydride, it breaks up into carbonic and propionic acids.

483. *Benzoic Acid* $C_6H_5.COOH$,

as obtained by sublimation, forms long, slender, white, non-transparent needles; the crystals obtained from the alcoholic or ethereal solution are usually larger. It melts at 121°, and sublimes at a somewhat higher temperature. It boils at 250°. The vapours have a characteristic smell and an irritating effect on the respiratory organs. Benzoic acid dissolves at 100° in about 12 parts, and at 0° in 607 parts of water; it is more largely soluble in alcohol and in ether. The acid when boiled with water is largely volatilized with the steam; what remains undissolved melts into a liquid. Benzoic acid vapour, when passed through a red-hot tube filled with pumice-stone, or, what is better, fragments of caustic lime, breaks up, substantially, into carbonic acid and *benzole* C_6H_6. Fuming sulphuric acid converts benzoic acid into sulphobenzoic $(C_6H_4)COOH.SO_2OH$; dilute nitric acid does not act; the strongest nitric acid produces nitrobenzoic; a mixture of nitric acid and oil of vitriol acting in the heat produces dinitrobenzoic acid.

Benzoates.—Benzoic acid, though monobasic, forms acid salts with potash and ammonia. All normal benzoates containing strong bases are soluble in water and generally also in alcohol. Neutral solutions of benzoates exhibit the following **Reactions**: *Hydrochloric acid*, from sufficiently concentrated solutions, precipitates benzoic acid. *Neutral ferric chloride* precipitates the acid completely in the form of a voluminous flesh-coloured salt, which is decomposed by ammonia like the succinate. *Acetate of lead* gives a flocculent precipitate soluble in excess of the precipitant. A mixture of *chloride of barium*, ammonia, and alcohol gives *no* precipitate.

Note.—The following among other acids, being similar to benzoic acid in appearance and in their solubilities, and, like it, sublimable and volatile with steam, are liable to be mistaken for it: Cinnamic $C_6H_5.C_2H_2COOH$; the three Toluic acids $C_6H_4.CH_3.COOH$; Alpha-toluic acid (phenyl- acetic) $C_6H_5.CH_2.COOH$.

484. *Malic Acid* $C_2H_3(OH).(COOH)_2$.

Malic acid is a deliquescent solid which crystallizes only with great difficulty. It is very easily soluble in water and in alcohol, but little soluble in ether. At 175°–180° it is decomposed into water and two isomeric acids $C_4H_4O_4$, of which the one, *maleic* acid, sublimes, while the other, fumaric acid, remains behind; at a higher temperature the *fumaric* acid also sublimes. Boiling nitric acid converts malic acid into oxalic. Malic acid when heated in a sealed-up tube with fuming hydriodic acid to 130°, is reduced to succinic acid. **Malates.**—Malic acid is dibasic. The normal malates of K, Na, NH_4 are uncrystallizable; the acid salts of the same radicles, especially the NH_4-salt, crystallize easily. The normal barium salt $C_4H_4BaO_5,H_2O$ is easily soluble in water; when the solution is boiled down, the anhydrous salt separates out as a crystalline powder. *Lime-water* in excess does not precipitate malic acid, not even on boiling; a more concentrated solution of the neutral lime-salt, when boiled down, deposits an almost insoluble salt $C_4H_4CaO_5,H_2O$ as a granular precipitate. A similar precipitate is obtained when a mixture of neutral alkaline malate and excess of chloride of calcium is being boiled down. This salt, when dissolved in the least quantity of hydrochloric acid, is reprecipitated from such solution on adding ammonia and boiling; but in presence of more considerable quantities of sal-ammoniac the salt remains dissolved. It may, however, in this case be precipitated by addition of 1 to 2 volumes of alcohol. A solution of the neutral lime salt in warm nitric acid deposits on cooling large rhombic crystals of the salt $C_4H_5Ca_{\frac{1}{2}}O_5+4H_2O$, which are soluble in 50 parts of water. *Acetate of lead* produces in a solution of malic acid or of malate of ammonia, a flocculent precipitate $C_4H_4PbO_5+2H_2O$, which becomes crystalline on standing. When the mixture is boiled the precipitate fuses into a resin-like liquid. A part of the salt dissolves in the hot liquid and crystallizes out on cooling, in slender needles. The fusion-phenomenon comes out clearly only with a *pure* precipitate. Even recently precipitated malate of lead is very sparingly soluble in ammonia. (Comp. tartaric and citric acids.) The *silver salt* is a crystalline precipitate which blackens on exposure to the light, and on boiling.

485. *Tartaric Acid* $C_2H_2(OH)_2.(COOH)_2$

forms hard colourless crystals soluble in about half their weight of cold and in less of hot water, soluble also in alcohol but insoluble in ether. Tartaric acid melts at 170°–180° and gets gradually changed into its isomer metatartaric acid; on continued heating it undergoes further changes, and passes at last into the anhydride $C_4H_4O_5$ which is insoluble in water, and which, when more strongly heated, undergoes a complex decomposition. The ordinary oxidizing agents, such as aqueous chromic acid, binoxide of manganese and sulphuric acid, etc., produce carbonic and formic acids. By the action of oil of vitriol and of nitric acid in the heat tartaric acid is destroyed. When heated in a sealed-up tube to 130° with fuming hydriodic acid, it is reduced, first to malic and then to succinic acid.

Tartrates.—Tartaric acid is dibasic. The alkaline salts are soluble; most other tartrates are insoluble in water but soluble in mineral acids, and often also in caustic alkali. The most characteristic tartrates are the acid potash salt $C_4H_5KO_6$ (cream of tartar), and the normal lime salt $C_4H_4CaO_6.4H_2O$. The former is obtained from the solution of the acid by half-way saturation with potash; from that of the normal potash salt, by addition of acetic acid; from that of any other neutral tartrate, by addition of acetate of potash and acetic acid—as a crystalline precipitate soluble in 235 parts of cold water. Its formation is promoted by stirring, and its quantity increased by addition of alcohol.

The *lime* salt is formed on addition of excess of lime-water to a solution of the acid, or of excess of chloride of calcium to one of neutral alkaline tartrate, as a white precipitate which on standing becomes crystalline. The precipitate, especially as long as it is amorphous, dissolves in cold concentrated caustic potash, forming a solution which on boiling deposits a gelatinous precipitate; it is also soluble in concentrated sal-ammoniac solution. It also dissolves in hydrochloric, nitric, acetic, and in tartaric acids. Recently precipitated washed tartrate of *lead* is soluble in aqueous ammonia. Of double tartrates the one known as '*tartar emetic*' $C_4H_4(SbO)KO_6.\frac{1}{2}H_2O$ must be mentioned as exhibiting peculiar reactions. This salt is prepared by boiling oxide of antimony and cream of tartar with water. It crystallizes in transparent tetra-hedra soluble in 14·5 parts of cold and in 1·9 parts of boiling water. From a solution of tartar-emetic, mineral acids precipitate a white salt soluble in excess of these acids and in tartaric acid; solutions of Ba-, Sr-, Ca-, Cd-, Pb-, Ag- salts produce precipitates of the composition of tartar-emetics in which the K is replaced by the metallic radicle of the precipitant.

Note.—What, in the above, has been called 'tartaric acid,' is only one of a group of isomers, which comprises the following modifications: (1) Dextro-tartaric acid, so called because it turns the plane of polarized light to the right (this is the ordinary commercial acid): (2) Lævo-tartaric- which turns that plane to the left; (3) Racemic acid, which is formed by the union of (1) and (2), and is optically inactive; (4) Inactive tartaric- not decomposible into (1)+(2); (5) Metatartaric acid. Of these the first four are almost identical in their chemical properties; the fifth differs from the others by the greater solubility of its salts.

486. *Citric acid* $C_3H_4(OH).(COOH)_3$

forms large colourless transparent crystals (of the composition $C_6H_8O_7.H_2O$*) soluble in $\frac{3}{4}$ part of cold and $\frac{1}{2}$ part of hot water, readily soluble also in alcohol, but insoluble in ether. The crystals melt at about 100°; at 175° the acid is decomposed, substantially into water and aconitic acid $C_6H_6O_6$. On continued heating, this acid is decomposed in its turn, and a liquid distils over containing itaconic and citraconic acids (both $C_5H_6O_4$). Citric acid is easily attacked by oxidizing agents. When the aqueous solution is heated with binoxide of manganese, acetone is produced along with other products. If dilute sulphuric acid is added, formic acid also is formed. Boiling concentrated nitric acid produces oxalic and acetic acids. **Citrates.**—Citric acid is tribasic. Its alkaline salts, inclusive of the *acid potash salts*, are all easily soluble in water. A solution of the acid, when mixed with excess of *lime-water*, gives *no* precipitate in the cold; on long-continued boiling, however, a white precipitate is formed which mostly disappears on cooling. *Chloride of calcium*, when added in *excess* to a solution of tribasic citrate of potash or soda, produces at once a precipitate of $C_6H_5O_7Ca_{\frac{3}{2}}.2H_2O$ which is *insoluble* in cold *caustic potash*, but soluble in large quantities of *sal-ammoniac.* When this solution is boiled, the lime salt re-appears in a crystalline form which is no longer soluble in sal-ammoniac. The normal *ammonium* salt is not precipitated by chloride of calcium in the cold; but on boiling the crystalline salt named is separated out. Excess of *baryta-water* when added to a solution of citric acid, or of *acetate of baryta* when added to a solution of alkaline citrate, produces an amorphous precipitate $C_6H_5Ba_{\frac{3}{2}}O_7.3\frac{1}{2}H_2O$. In dilute solutions the precipitate does not appear, but if the mixture is heated, an amorphous precipitate separates out, which soon passes into a crystalline salt $C_6H_5Ba_{\frac{3}{2}}O_7.\frac{5}{2}H_2O$. When this, or the amorphous, salt is heated with acetate of baryta on a water-bath for about two hours, characteristic klinorhombic prisms of a new salt $C_6H_5Ba_{\frac{3}{2}}O_7+\frac{7}{4}H_2O$ are formed. —(*H. Kämmerer.*) *Acetate of lead* forms an amorphous precipitate which, after removal of the other products by washing, dissolves in aqueous ammonia.

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* *Warrington*, Chem. Soc. Journ. Oct. 1875.

487. *Detection of Metals in presence of Malic, Tartaric, and Citric Acid.*

These acids (like a number of other non-volatile organic substances, for instance the sugars) prevent the precipitation, by ammonia, of iron, aluminium, manganese, copper, and some other basic metallic radicles. These substances, however, do not interfere with the normal action of sulphuretted hydrogen or sulphide of ammonium. Alkaline citrates have the power of dissolving, and consequently may prevent the precipitation of, sulphate of baryta, and of a great many other metallic salts which are insoluble in water and ordinary salt-solutions. The substances referred to may be destroyed by incineration, or removed by treatment with oil of vitriol in the heat.

Ultimate Analysis of Carbon Compounds.

488. (1) **Detection of combined Carbon.**—In many non-volatile compounds of carbon, the presence of this element can be proved by exposing the substances to a red-heat in (practical) absence of air, when very often part of the carbon separates out as *charcoal* which can be recognised by its blackness and combustibility. A residue left after the prolonged exposure of a substance to a red heat can contain combined carbon in only a very few forms, viz.: as carbonate, cyanide, cyanate, sulphocyanate—which classes of salts are all easily recognised by their specific reactions.

A *more general* method of carbon-detection, which applies to all those substances which are either non-volatile in themselves, or become fixed by the action of *oil of vitriol*, is to heat the substance with excess of oil of vitriol and *chromic acid* (in a retort, the neck of which is turned upwards), when all carbon-compounds present are completely burned and have their carbon converted into *carbonic acid*, which is easily identified by the precipitates which it forms in *lime-water* and in *baryta-water*. In using the latter reagent, which is more delicate than the former, we must take care not to mistake sulphate or sulphite of baryta for carbonate; but the carbonic acid, given as $BaCO_3$, is easily distinguished from the other two by its being re-liberated as a gas on successive addition of chromate of potash and of hydrochloric acid. The method given is particularly handy for seeing whether a substance, from which carbonic or other volatile carbon-acids have already been expelled by dilute sulphuric acid, still contains carbon in other states of combination. An *absolutely general* method of carbon-detection may be founded upon the fact that all carbon compounds when burned with excess of *oxide of copper* in a combustion-tube—which should be done in such a manner that no volatile products can leave the tube without having first passed over a sufficiently long layer of red-hot granulated oxide—are completely changed so, that the carbon is converted into carbon-dioxide which escapes, and can be recognised by lime- or baryta-water—*i.e.* if it has not been retained by potash, soda, baryta, strontia, or lime contained in the substance itself. This method works best with such substances as contain carbon, hydrogen, and oxygen only. If nitrogen is present, this element is partly liberated as nitric oxide, which subsequently passes into and escapes as nitrous acid or peroxide of nitrogen; halogens, if present, cause the formation of sublimates of their cuprous compounds; *sulphur* goes off partly as *sulphurous acid.* These inconveniences are all avoided, if, instead of oxide of copper, fused *chromate of lead* is used as a source of oxygen, and the volatile products, before being allowed to leave the tube, are passed, first through a column of red-hot granulated oxide of copper and then through one of red-hot *copper-gauze.* The chromate of lead retains the halogens as lead compounds, and the sulphur as sulphate of lead, while it decomposes any metallic carbonates completely; the metallic copper reduces the nitrogen-oxides to free nitrogen.

489. (2) **Detection of Hydrogen.**—In the combustion of a carbon compound containing hydrogen, this element goes off as vapour of water, which, even if formed in small quantities, when the products are passed through a cold narrow tube, condenses partially in visible globules. A

positive result of course goes for nothing, unless it is proved that the materials and reagents used were anhydrous. The essential presence of hydrogen in an organic substance can be satisfactorily proved only by quantitative analysis. (3) Regarding **Nitrogen**, see § 399.

490. (4) **Detection of other elements*** than C, H, N, O. A satisfactory and almost absolutely general method for the solution of this problem was discovered some years ago by *Carius*. His method is founded upon the fact that almost all organic substances when heated in sealed-up tubes with an excess of sufficiently strong nitric acid for a sufficient time, are completely burned, *i.e.* changed so, that while the carbon and hydrogen are converted into CO_2 and H_2O respectively, the other elements are changed so as if, at some stage of the operation, they had been present in the free state. The strength of acid, and the temperature to be used, and the length of time required for a complete decomposition, vary according to the nature of the substance under operation. An acid of 1·4 spec. gravity is strong enough in all cases; the temperature required varies from 120°–180°; the time of heating from 2 to 10 hours. There are, however, a number of substances which cannot be completely burned by even 1·4 acid acting at the highest practicable temperature. Many of these, perhaps the majority, can be burned by addition to the nitric acid of a quantity of bichromate of potash which is calculated so that its available oxygen alone (O_3 for Cr_2O_6) would be sufficient for a complete combustion. Supposing the proper conditions to have been established, and the operation to have been successfully executed, then the several elements are obtained ultimately in the following forms: C as CO_2; H as H_2O; Cl, Br, as Cl_2, Br_2 respectively; I partly as I_2, partly as I_2O_5†; S, P, As, Sb as hydrates of SO_3, P_2O_5, As_2O_5, Sb_2O_5 respectively; Sn as metastannic acid; the rest of the metals as nitrates.

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* Compare the appendices on organic compounds in the chapters on N, S, P, halogens.

† If nitrate of silver was added before heating, the halogens are more readily eliminated as silver salts.

491. *Modus operandi.*—A sound piece of combustion-tubing is closed at one end, and into it is introduced from 0·2 to 0·5 grammes of the substance, either directly or (if it is liable to be decomposed by the nitric acid in the cold, with evolution of gaseous products) after having been previously sealed up in a very thin-walled hard glass bulb or cylinder. The requisite quantity of nitric acid (about 20 times the theoretical quantity, supposing the acid to be reduced to $H_2O+N_2O_2$), is now introduced and the open end drawn out so as to form a strong cone with a thick-walled capillary tube, 2 to 3 ctm. long at the end, which is then sealed up. The acid should not fill more than $\frac{1}{3}$ to $\frac{1}{2}$ of the tube, which is now slipped into a stout iron tube, and within this placed into an air-bath and brought up to the requisite temperature, care being taken to place the air-bath so, that, if the tube should burst, the explosion can do no harm. When the oxidation is supposed to be completed, the tube is allowed to cool, taken out of the iron tube, wrapped up in a towel, and the tip softened in the flame of a Bunsen's lamp, so that the gases may break through the soft glass and *gradually* escape through the capillary canal. If the tube were opened so as to allow of a sudden escape of the accumulated gases, this would almost invariably lead to a dangerous explosion. We would warn students not to attempt their first operation of this kind otherwise than under the direction of an expert. The somewhat troublesome process of Carius need not of course be resorted to in all cases. Thus, for instance, many of the methods given for the detection of inorganic bases or acids apply as they are, or with only slight modification, to the case of the acids or bases to be searched for being in combination with organic alkalies and acids respectively. And in many cases in which organic substances must be removed to clear the road for the application of this or that analytical method, this can often be effected by easier methods than Carius's, *e.g.* by incineration, by treatment with oil of vitriol in the heat, or otherwise.

Detection of Metals in presence of large quantities of organic matter.

In the solution of this problem, which occasionally presents itself to the analyst, especially in forensic cases, it is generally necessary first to remove at least the bulk of the organic matter before the application of the ordinary analytical methods can be proceeded with. For the accomplishment of this we have mainly two methods. The one consists in this, that after having extracted from the mass of organic matter the metallic compounds assumed to be present by means of some appropriate reagent, such as hydrochloric acid for instance, we subject the liquor thus obtained to

492. Dialysis, when, as a rule, the metallic compounds, being '*crystalloids*,' pass through the septum, while just those organic substances which would more seriously interfere with the application of metal-precipitants, being most of them '*colloids*,' remain behind. The other method is, by means of some strong oxidizing agent, to *destroy* the organic substances.

493. In the case of viscid or dark-coloured aqueous liquids, such as are obtained by exhausting a mass of animal or vegetable matter (for instance, the contents of a stomach) with water or hydrochloric acid, this can generally be accomplished by treating the liquids in the cold or in the heat with a current of chlorine. The liquids thereby are, as a rule, rendered sufficiently thin and colourless for being filtered and examined with reagents. Solid or semi-solid mixtures may be treated as follows: mix the substance with about twice its bulk of hydrochloric of 1·12 spec. gravity, heat the mixture on a water-bath, and add successive small portions of chlorate of potash—taking care always to keep the acid in considerable excess—until the liquid has become thin, filterable, and nearly or quite colourless.

Whether free chlorine or chlorine-oxides were used for the destruction of the organic matter, expel the excess of the gaseous oxidants by evaporation at a gentle heat, allow to cool, when a quantity of fat will as a rule separate out, and filter. The filtrate, although by no means free from organic matter, is now in a fit state to be examined by the systematic application of the ordinary metal-precipitants; it is however to be observed that the precipitates will form more slowly than they would in pure liquids, and will contain, or may even entirely consist of, organic substances. This holds more especially of the sulphuretted-hydrogen precipitate, which, even in absence of metals, is as a rule rather copious. The examination of this precipitate may be conducted as follows:

(1.) Treat the precipitate, after removal of the last trace of adhering chlorides by washing, with strong nitric acid in a porcelain dish, and keep at a gentle heat until the bulk of the organic matter may be supposed to be destroyed, and the decomposible sulphides oxidized. If sulphide of mercury should be present this will remain undissolved, and must, after dilution with water, be removed by filtration. Now super-saturate the acid by addition of *pure carbonate of soda*, evaporate cautiously to dryness, and then continue heating, until the last trace of organic matter is completely burned by the fused nitrate, and the whole converted into a colourless liquid. The combustion will proceed quietly and without any explosion, provided that there was a sufficient excess of carbonate and nitrate of soda present—a most important point, which should always be made sure of by a preliminary experimental fusion of a small portion of the mass. The product contains all the heavy metals that can be present as oxides or sodium salts of metallic acids (thus the copper is present as CuO, the arsenic, antimony, and tin as sodium-salts of As_2O_5, Sb_2O_5, SnO_2 respectively), *i.e.*

in forms accessible to well-known processes of analysis.—(*Wöhler.*)

(2.) *Fresenius* recommends the following method: Dissolve the sulphides in fuming nitric acid of 1·5 spec. gravity and evaporate at a gentle heat to dryness. Mix the residue with oil of vitriol, and heat, first for 2 to 3 hours to 100°, and at last to 170°, until a specimen of the mass, when mixed with water, yields a colourless solution. This process is often found to be accelerated by the occasional addition of bits of Swedish filter-paper. At last dilute with water and filter; the filtrate, which is now quite free from organic matter, contains the arsenic as arsenious acid, the other metals as sulphates. The residue consists of charcoal, mixed possibly with sulphide of mercury and the sulphates of lead, tin, and bismuth.

IX. HYDROGEN.

494. 'Free' Hydrogen H_2 is a colourless, inodorous, tasteless permanent gas of the spec. grav. $0{\cdot}0698 = \frac{1}{14{\cdot}47}$ (Air = 1), soluble in 49 times its volume of water at 15°. There is no specific absorbent or characteristic reagent for hydrogen, by means of which an admixture of the gas in other gases could be recognised by qualitative testing; in gas analysis it is recognised by its combustibility with oxygen, and by the fact that in such combustion 1 vol. of it combines with ½ volume of oxygen to form 1 volume of steam, which, on cooling, condenses into practically 0 volumes of liquid water.

495. Hydrogen Compounds, from the stand-point of the analyst, may be divided into two classes (which however to a considerable extent overlap each other); namely, (1) *Hydrates, i.e.* compounds containing the elements H_2+O combined with some residue in such a manner, that, without effecting a dissociation of that remainder, the H_2+O can be eliminated as H_2O, either by the effect of heat alone, or by the combined effect of heat and a fixed acid or basic oxide. (2) *Combustible Hydrides:* these, or at least the majority of these, when burned with oxide of copper or chromate of lead in a combustion tube, give up their hydrogen as water. Our methods for detecting combined hydrogen all come to this, that we eliminate the hydrogen as *water*, and identify it in this form.

Water.

496. Any clean specimen of common 'sweet' water differs from the ideal substance H_2O only in so far as it holds in solution small quantities of certain impurities, viz. of the gases of the atmosphere (O_2, N_2, CO_2, traces of NH_3) and of a complex of metallic salts formed by the union of the bases CaO, MgO, FeO, K_2O, Na_2O with hydrochloric, sulphuric, carbonic, silicic acids, and sometimes also phosphoric acid. The relative proportions of these constituents vary very much in different kinds of water. Some natural waters are extremely pure; thus, for instance, the water of Loch Katrine, used in Glasgow for domestic purposes, may safely be said to be a better approximation to real H_2O than even the best of our so-called pure reagents are to the ideal substances of which they bear the names. To purify a natural water, we subject it to distillation: *i.e.* we raise from it a supply of *dry* steam, and condense the steam in a copper or block-tin (or, what is better, a silver or platinum) tube,* kept cool by immersion in a cold water bath. Such 'distilled water' can contain no impurities but dissolved atmospheric gases and perhaps traces of volatile organic matter, which however do not interfere with most of the analytical applications of the substance. If, for particular purposes, air-free water is required, this can be procured by boiling distilled water in a glass, or, what is better, a copper, flask until it begins to 'bump,' and then allowing it to cool in absence of air. The traces of organic matter left after distillation can, according to *Stas*, be destroyed by prolonged digestion and subsequent distillation, with *manganate of potash* and re-distillation with phosphoric acid to remove the ammonia.

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* Glass tubes are strongly attacked, and must therefore not be used.

497. *Properties.*—Pure water is a tasteless inodorous liquid, perfectly neutral to litmus and turmeric, and, of course, without action on any aqueous reagent, which is not, like bismuth or antimony salts, visibly decomposed on addition of water. Small quantities appear colourless, but when viewed in masses it is found to be blue. Perfectly pure water being easily procured in any quantity, it is used as a standard of comparison in the determination of certain physical properties (densities, specific heats, etc.) of substances, and for defining the fixed points of our thermometers. Hence it is only a repetition of the definitions of these points to say that water freezes at 0° and, under a pressure of 760 mm., boils at 100°. 1091 volumes[*] of ice of 0°, by absorbing 79·25 units of heat (per unit-weight) give 1000 volumes of liquid water of 0°, which when gradually heated first contract to assume their maximum density at +4°, and then expand in accordance with the following table :—

t= 0°	4°	8°	15°	50°	100°
vol.=1000	999·88	999·99	1000·7	1011·77	1043·0

The maximum tension of vapour of water at t° equals the pressure of P mm. of mercury of 0° :

t = 0°	10°	15°	20°	30°	50°	100°
P=4·6	9·17	12·7	17·39	31·55	91·98	760 mm.

498. The identification of water, if not rendered unnecessary by the known history of the specimen, is easily effected by the observation of its negative, general, and chemical properties, provided that there is a sufficiency of material. But if the specimen given was only small the problem of giving a rigorous proof of its identity would not just be easy. Probably the best method—in addition to the well-known negative qualitative tests—would probably be to institute a perfectly *direct* comparison of the substance with an authentic specimen of H_2O, with regard to expansion by heat (especially the situation of the point of maximum density), freezing point, and vapour tensions; and to show that the substance, when burned with oxide of copper, yielded nothing but itself without loss or increase of weight.

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[*] *Bunsen.*

499. *Examination of a substance for Water.*

(a) *Solutions.*—In order to see if a given solution is an *aqueous* one, we subject it to distillation from an oil-bath kept at a temperature at which the residue is not apparently decomposed, and examine the distillate. Of the many cases that may present themselves, the following are the most important: (1) The distillate is *pure water* (*vide* supra); (2) It is an aqueous solution of volatile acids or alkalies. In this case re-distillation with respectively caustic soda or phosphoric acid would yield pure water. (3) The distillate contains or consists of other volatile substances, than those mentioned in (2). If, in such a case, the distillate consists at least partially of water, it is generally possible to separate out some of it by fractional distillation.

(b) **Solids.**—A solid, say for instance a salt, may contain water in three forms: (1) as a mechanical admixture; (2) in loose molecular combination (*e.g.* as crystal-water); (3) in atomic combination, *i.e.* in the form of hydrates properly so called. It being impossible, by purely experimental methods, to distinguish hygroscopic from loosely combined water we at once pass to **case** (2). Most of the compounds of this class are dehydrated at 100°–110°, and, if the residue is not volatile at these temperatures, can thus easily be analysed. The water, if its quantity is not too small, may be collected and identified. This however is rarely done; the proof of the volatilized matter being water, if not rendered unnecessary by the known history of the substance, being generally established indirectly, either by showing that the quantities of the several elements present in the substance besides those of H_2O have remained unchanged in the process, or else by showing that the residue, when treated with pure water, is re-converted into the original substance. **Case** (3).—*Metallic Hydrates* may be classified as follows: (1) Such as are easily dehydrated at or below a dull red-heat; exx.: the hydrates of the oxides of the *copper*, *arsenic*, and *iron groups* and of *magnesium*. The anhydrides of these hydrates (except MgO and As_2O_5) do not recombine with water. (2) Such as can be dehydrated only by prolonged exposure to a bright red heat; exx.: the hydrates of *strontia* and *lime*; these two oxides greedily recombine with water. (3) Such as *cannot* be dehydrated by mere heating; exx.: the hydrates of *baryta*, *potash*, *soda*. From these the water can be expelled and quantitatively determined by fusion with an excess of anhydrous *bichromate of potash*, or of *borax-glass*, or of silica. Ex.: $2KHO + K_2OCr_2O_6 = 2K_2OCrO_3 + H_2O$. *Hydrated acids.*—Many di- and polybasic acids can be dehydrated by mere heating; but apart from the few cases in which the anhydride is absolutely stable in the heat (like silica, tungstic trioxide) these processes cannot be discounted in analysis. The determination of the water in an acid is usually effected, either by evaporating a known weight of the acid with a known weight of (excess of) some anhydrous oxide, like oxide of lead, and weighing the residue; or else by comparing the formula of the acid with the formula of a well-defined anhydrous salt. Example: acetic acid$=C_2H_4O_2$; acetate of silver$=C_2H_3AgO_2$; hence, $C_2H_4O_2$ contains $\frac{1}{2}H_2O$ of potential water.

500. *The Examination for Impurities*

of a water meant to be used for chemical or domestic purposes may be conducted as follows:—

1. See that the water is clear, colourless, inodorous, not infected with a bad taste, and neutral to test-paper.

2. Measure out quantities of, say 100 cc., in test-glasses, apply the well-known reagents for chlorine, sulphuric acid, lime, heavy metals, etc., and note the effects. In the case of negative results, concentrate a large quantity of the water by evaporation in a platinum or silver dish (or in default of these in a Berlin porcelain basin—*not* in glass) to $\frac{1}{10}$th or $\frac{1}{20}$th of its original volume and repeat the tests. Or, what is better :

3. Evaporate a known volume, 100–500 cc., in a tared platinum basin to dryness. Perfectly pure water of course leaves no residue ; but practically, even with distilled water, we must tolerate, say 2 milligrammes per litre. If there is an appreciable residue, dissolve it in a little pure water or very dilute hydrochloric acid and apply the tests (2). *Note.*—The most delicate reagent for lime and magnesia salts is a solution of '*sapo mollis*' (Pharmacop. Lond.) in 50 per cent. alcohol (15 grms. per litre). To use this reagent, first determine the (small) volume of it which must be added to 100 cc. of *pure* water to produce a mixture which, when shaken, yields a thick relatively permanent froth. If 100 cc. of the water under examination requires more than that minimum volume of soap-solution to exhibit the same phenomenon, this indicates the presence of lime or magnesia salts, and the excess is proportional to the joint number of equivalents of lime and magnesia present, and hence a measure for the '*hardness*' of the water.

4. *Test for Ammonia* by adding, to 100 cc., two or three drops of *mercuric chloride* and one drop of *carbonate of potash*. If it was previously ascertained that the latter reagent for itself produces no visible effect, a *white precipitate* formed proves the presence of ammonia. Or else use *Nessler's* reagent according to § 266. A more refined method is to distil ½ litre of the water with about 1 gramme of ignited carbonate of soda, and to examine the first 50 cc. of distillate. If *Nessler's* reagent be used, the ammonia may be determined quantitatively by ascertaining how many centi-milligrammes of

ammonia have to be added to 50 cc. of *pure* water to produce a mixture which, on addition of say 1 cc. of '*Nessler*,' produces the same depth of colour as the 50 cc. of the distillate obtained from the water. To determine

5. The '*Albuminoid*' *Nitrogen*, a most important element in the valuation of a drinking water, continue the above distillation until the last drops of distillate no longer contain any ammonia, and then see if an additional quantity of this base can be produced by resuming the distillation after addition of permanganate of potash and caustic potash. The ammonia which now comes over must owe its origin to nitrogenous organic matter in the water,—if the reagents were perfectly pure, which must be ascertained by an experiment *au blanc* with *pure* water.

6. Test for *nitrous* and *nitric acids* by applying the refined methods of examination given in §§ 387 and 393, either to the water in its natural state, or to the residue obtained on concentrating a large quantity after addition of some carbonate of potash.

X. OXYGEN.

ELEMENTARY oxygen exists in two allotropic modifications, viz., as *ordinary oxygen* O_2, and as *Ozone* O_3. (Regarding the latter, see § 507.)

501. Ordinary Oxygen is an inodorous, tasteless, colourless, permanent gas of the spec. gravity 1·1057 (Air=1). Coefficient of absorption at 15°, for water=0·030; for alcohol 0·284 (volumes reduced to 0° and the prevailing pressure). It is largely absorbed, chemically, by a solution of *alkaline pyrogallate* with formation of a dark-coloured liquid; by a solution of *cuprous chloride* in hydrochloric acid or in ammonia; by moist *phosphorus*, and at a red heat by *metallic copper*. Oxygen and *nitric* oxide, when mixed together, unite at once with formation of brown-red fumes of N_2O_3 and N_2O_4. This is quite a specific reaction for oxygen. The well-known property of inflaming a glowing splinter is exhibited not only by approximately pure oxygen but by any mixture of oxygen and nitrogen containing at least 50 per cent. by volume of the former gas. This phenomenon is also exhibited by *nitrous oxide*, which, however, is easily distinguished from oxygen by its not acting on nitric oxide.

502. *The detection of combined Oxygen*

is one of those problems of ultimate analysis which have not yet found even a relatively general solution. And, if we had such a method, unless it were very easy of execution, it would be of little use to the practical analyst. Because his object generally is to ascertain the *nature* of the substance under examination, and as ninety-nine out of every hundred substances contain oxygen, the evidence afforded by the proof of the presence of this element in a given substance would be of little value. But the problem of ascertaining whether or not a given definite compound is or is not an oxide, and, if it is, of determining its percentage of oxygen, is of the highest possible interest to the investigator. We shall therefore here give a short sketch of the principal methods we possess for its solution. These may be classified as follows:—(1) Direct synthetical methods; (2) Analytical methods proper, *i.e.* such as are applicable to individual *specimens;* (3) Indirect methods which, though inapplicable to the *specimen*, may serve to determine the composition of the *species*.

503. (1) **Direct Synthesis** from the elements has served, or helped, to establish the compositions of the most important binary oxides; for instance those of H_2O, SO_2, CO, CO_2. The oxygenated nature of these compounds is as well established as that of O_2 itself; hence, if in the investigation of a substance we can, without introducing oxygen from without, produce from it one of them, this amounts to a demonstration of the presence of oxygen in the original substance.

504. (2) Of the **Analytical Methods** some are *direct* and susceptible of qualitative application, while others are *indirect* and purely quantitative. In the former, the oxygen is actually eliminated as such, or in the form of a well-defined oxide. Such elimination may be effected—(a) *By the effect of Heat alone.* This method is very widely applicable theoretically, inasmuch as most compounds, by the application of an intense heat, can be caused to dissociate, but practically it is available only for the small number of substances which, like the following, lose oxygen at a red heat. A red heat reduces completely the oxides of *gold*, *platinum*, *silver*, *mercury;* it reduces incompletely the higher oxides of *manganese* to Mn_3O_4; those of *chromium* to Cr_2O_3; those of *lead* to PbO; those of *barium* to BaO. Other oxides which can be conveniently deoxygenated by heating are: all chlorates and perchlorates, some iodates (including I_2O_5), and periodates. Nitrates, chromates, permanganates, and iodates and periodates generally, when exposed to a red heat, lose in general only a *part* of the oxygen of the acid even. The oxygen liberated in such cases is easily identified, and if nothing else goes off besides the oxygen, it may be determined quantitatively by identifying it with the loss of weight suffered by the substance.

(b) *By the joint effect of Heat and Reagents.* The reagents usually employed are: hydrogen, carbon, carbon and chlorine, metallic copper. **Hydrogen** at a red heat reduces completely the oxides of arsenic, antimony, tin, lead, bismuth, copper, cadmium (?), nickel, cobalt, iron; it reduces to lower oxides the higher oxides of manganese (to MnO); those of uranium (to UO_2); it reduces incompletely oxide of zinc. It does not reduce at all the oxides $R''O$ or R'_2O of the barium and potassium groups, alumina, silica. The water formed in these reductions may be condensed, partly as such (for identification), the rest by means of chloride of calcium or oil of vitriol, and its quantity be determined by direct weighing. All oxides reducible by hydrogen can be reduced also by *carbonic oxide*, with formation of *carbonic acid*, which product, in the case of small quantities of oxygen, is more easily identified than water. **Metallic copper** reduces at a red heat all oxides of nitrogen to N_2 with formation of oxide of copper, which, in its turn, can be reduced by hydrogen or carbonic oxide, and thus be identified as an oxide. Metallic copper does not act on the oxides H_2O, CO, CO_2; hence it may serve to determine oxygen given as O_2 or as N_2O_x beside the oxides named.

Carbon at a red or white heat reduces most of those oxides which resist the action of hydrogen; but these reactions, on account of practical difficulties, are not of much avail in exact analytical experiments. **Carbon and chlorine**, when applied conjointly at a sufficiently high temperature, are capable of reducing almost all binary oxides; the oxygen being converted into carbonic oxide and acid, while the radicle combines with the chlorine. In this way silica and alumina, for instance, may be deoxygenated. There is no reason, theoretically, why the carbon oxides should not be separately determined, and their oxygen, *i.e.* the oxygen of the substance, be calculated; but the proper *modus operandi* has not yet been worked out. The quantity of oxygen eliminated is therefore always determined by the indirect methods to be given below.

505. (3) Of the *indirect quantitative* methods we shall give two as being of comparatively wide applicability. The one, which chiefly applies to metallic oxides, consists in converting the oxide into a chloride—(1) by heating the oxide in a current of dry hydrochloric acid; or (2) by dissolving it in the aqueous acid, evaporating to dryness and dehydrating the residue in HCl gas; or (3) by means of carbon and chlorine,—and determining the quantities corresponding to one another of oxide S, chloride C, and chlorine in the chloride c. Obviously the oxygen in S parts of substance $= S - (C - c)$. These quantities, however, can, as a rule, not be obtained in a strictly synthetical manner, but must be procured indirectly by determining, for two known quantities of *ready made* chloride, the quantities of, respectively, oxide and chlorine which can be obtained from them. It is also to be observed that the processes (1) and (2) do not always eliminate the whole of the oxygen, but stop after formation of a certain oxychloride. *The second method* is to determine in a given weight of the substance all that which is *not* oxygen and ascertain the weight of the latter by difference. This method is always employed in the ultimate analysis of carbon compounds. It is, however, easily seen that it cannot possibly be very exact, and that, if in the qualitative analysis any element was overlooked, it is put down as so much oxygen. It was in consequence of such an oversight that *taurine* was for a long time supposed to be $C_2H_7NO_5$ until *Redtenbacher* showed that the substance contains *sulphur*, and its real composition is $C_2H_7NSO_3$; SO_3 being quantitatively$=O_5$.

506. Indirect Methods of Investigation.—In a great number of the best-known oxides the presence and proportion of oxygen were determined, at least originally, not by mere experiment but by a combination of experiment and theory. Thus, for instance, the composition of the oxide '*Magnesia*' was determined in something like the following manner: A weighed quantity of the base was converted into sulphate by treatment with sulphuric acid, the excess of the latter and the water driven off by heat and the weight of the sulphate determined. 1 part of oxide gave 3·00 parts of sulphate. In the whole of the process nothing but water and sulphuric acid was observed to go off, and the sulphate when decomposed by an intense heat yielded only SO_2 and O, but no water. Hence the matter gained by the oxide must consist entirely of the elements of anhydrous sulphuric acid, a residue which by previous experiments had been proved to be SO_3, and the sulphate consequently have the composition $M.SO_3$, where $M=40$ parts of magnesia (for $O=16$, $S=32$). To ascertain the constitution of M, the sulphate of magnesia was compared with the sulphate of oxide of zinc, which is extremely similar to it in its properties and reactions. This comparison showed that for every hydrate and double salt of the zinc salt there was a corresponding isomorphous and otherwise very similar salt of magnesia, and that in all cases the difference in composition consisted only in this, that where the zinc salt contained 81 parts of zinc-oxide, the magnesia salt contained $M=40$ parts of magnesia. Now the 81 of oxide of zinc were known by direct synthesis to contain $O=16$ parts of oxygen, *i.e.* to be ZnO, and hence it was concluded that the equivalent quantity of magnesia also must contain $O=16$ parts of oxygen combined with $40-16=24=Mg$ parts of a then unknown metallic radicle. This conclusion subsequently was amply confirmed by the analysis of the chloride and by other experiences. We shall now pass to a case in which a similar method and similar reasoning, when subsequently tested by direct experiment, proved fallacious. The composition of yellow oxide of *uranium* was originally deduced from the ratios in certain uranic salts, of oxide to acid, on the assumption of these salts being similar in their constitution to what were assumed to be the corresponding salts of ferric oxide. The comparisons showed that, in regard to corresponding salts, 288 parts of uranic oxide were equivalent to, *i.e.* 'saturated,' the same quantity of acid as 53·3 parts of ferric oxide known to contain $O=16$ parts of oxygen combined with $fe=37{\cdot}3$ parts of metal. Hence it was concluded that the 288 parts of uranic oxide likewise must contain 16 parts of oxygen combined with $R=272$ parts of a metallic radicle which was called 'uranium.' The result was confirmed by the experience that 288 parts of uranic oxide (just like feO parts of oxide of iron) when ignited in hydrogen lost 16 parts of oxygen and left $R=272$ parts of residue. And as the atomic weight of iron was assumed to be $=Fe=\frac{3}{2}\,fe$, the atomic weight of uranium was put down at $U=\frac{3}{2}R=408$.

Thus, for instance, the formula of the most stable sulphate of uranic oxide was assumed to be $U_2O_3.3SO_3$ in analogy with $Fe_2O_3.3SO_3$ (normal ferric sulphate). Everybody will admit that, allowing the supposed analogies, the reasoning was as good as the one employed in the case of the magnesia. The result, in fact, was universally adopted as correct until *Péligot* showed that the reputed metal, when ignited with charcoal in chlorine, yielded a chloride, containing, in combination with chlorine, a residue of which 60 parts could be converted by a virtual oxidation into 68 parts of the radicle 'U.' Thus the reputed element turned out to be an oxygenated radicle containing $O_2=32$ parts of oxygen in every $R=272$ parts: and the correct compositions of

The oxygenated radicle	The yellow oxide	The sulphate
were proved to be		
$R=rO_2$	$RO=rO_3$	$ROSO_3=rO_3.SO_3$

where r stands for 240 parts of the true element. This, as everybody knows, are our present formulæ for the three substances; until lately, however, the atomic weight of uranium was supposed to be$=\frac{1}{2}r=120=$'U,' so that, notwithstanding the great change in the meaning of the symbol 'U,' the yellow oxide remained a sesquioxide.

507. *Ozone* O_3

is formed when a current of electric sparks is passed through ordinary oxygen; $2O_3$ (4 vol.)$=3O_2$ (6 vol.) It is also produced in the slow oxidation of phosphorus in moist air. Ozone is known only as an admixture of ordinary oxygen.

Chemically it is characterised chiefly by the facility with which it passes into the more stable condition of O_2. The conversion can be brought about: (1) by temperatures exceeding 250°; (2) by contact with certain reagents capable of abstracting the third atom of oxygen in the molecule O_3. In these reactions ozone may act as an oxidizing or as a reducing agent. *Examples of oxidizing action.*—When ozone is shaken with mercury, the metal is partially oxidized and thereby becomes viscid ('draws tails'). *Iodide of potassium* solution absorbs ozone with formation of free *iodine* and *iodate;* on subsequent addition of hydrochloric acid, the whole quantity of iodine equivalent to the third atom of oxygen is liberated. $O_3+2HI=O_2+H_2O+I_2$. Ozone bleaches *indigo* and other vegetable colours by oxidation. It converts *sulphide of lead* into sulphate, finely divided *silver* into oxide and peroxide. *Example of a reduction.*—Ozone and peroxide of hydrogen mutually reduce each other thus: $H_2O_2+O_3=2O_2+H_2O$.

508. *Peroxide of Hydrogen* H_2O_2

is formed in the decomposition of the peroxides of potassium, sodium, and barium, by excess of dilute acids in the cold. Ex. $BaO_2+2HCl=BaCl_2+H_2O_2$. An aqueous solution of peroxide of hydrogen when dehydrated as far as possible by being kept *in vacuo* over oil of vitriol leaves a colourless syrupy residue of 1·45 spec. grav., not freezing at −30°, slightly volatile at ordinary temperatures, and miscible in all proportions with water. The *reactions* of peroxide of hydrogen are those of a loose compound of water and oxygen $H_2O.O$; it readily breaks up into the two constituents with evolution of heat. The decomposition can be effected: (1) By the action of heat; when once started in pure or in the concentrated aqueous peroxide, it continues by itself. (2) By the 'catalytic' action of finely divided *platinum*, *silver*, *charcoal*, and other substances. (3) By contact with certain *oxides*, the oxygen evolved in such cases being supplied, the one-half by the peroxide of hydrogen, the other by the oxide added. Ex.: $Ag_2O+H_2O_2=Ag_2+O_2+H_2O$. $MnO_2+H_2O_2$ (in presence of dilute sulphuric acid)$=MnO(SO_3)+H_2O+O_2$. In *dilute* solutions the presence of peroxide of hydrogen can be proved by the following tests: (1) Very dilute aqueous H_2O_2 does *not*, in itself, act on *iodide of potassium* (this distinguishes it from ozone); but it does so on addition of *ferrous sulphate*, through the transitory formation of ferric salt, with liberation of iodine. (2) It *decolorizes*, in presence of sulphuric acid, a solution of *permanganate* of potash. This reaction may serve for the quantitative determination of peroxide of hydrogen; Mn_2O_7 corresponds to $5H_2O_2$. (3) When an *excess* of peroxide of hydrogen is added to *chromic acid*, the latter is converted into a peculiar *intensely violet* compound, which, when the mixture is shaken with ether, passes into the ethereal layer. This is the most delicate test for H_2O_2. (4) It reduces *ferricyanide* of potassium to ferrocyanide.

SUMMARY of Operations available for the Detection of the *Non-Metallic* constituents of Substance in general, and of the *Inorganic Acids* in a Mixture of Metallic Salts in particular.*

A.—For Solids.

509. I. *The Substance is gradually heated to higher and higher temperatures in a sublimation tube.*

A sublimate of *Water*	indicates the presence of *hydrates*.
Evolution of *Ammonia*:	the presence of certain *ammonia* salts.
,, *Oxygen*:	the presence of salts of oxygen-acids of the *Halogens*, *Nitrates*, etc.
Formation of *Charcoal*:	*Organic* substances.

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* For details of operations and qualifications of statements see the respective chapters.

510. II. *The Substance is heated in a sublimation tube with* **Soda-Lime.**

The evolution of *Ammonia* proves the presence of combined nitrogen, and points to *ammonia salts*, *amides*, *nitrides*, and, in presence of organic matter, to *nitrates* or *nitrites*.

511. III. *The Substance is heated with* **Carbonate of Soda,**

(*a.*) on *charcoal* in the reducing flame: *Sulphur* in any state of combination is reduced to *hepar*, recognised by its action on *metallic silver*.

(*b.*) At the end of a *platinum wire* in the oxidizing flame: this may lead to the detection of *silica* (or of manganese).

512. IV. *The Substance is treated with* **Oil of Vitriol** *in a test-tube, first in the cold, then in the heat.*

(1.) If there is *no gas or vapour* evolved: this shows the absence of considerable quantities of volatile acids and *carbon* compounds.

(2.) Evolution of *oxygen* suggests the presence of chromic, permanganic acid, metallic peroxides, or other forms of loosely combined oxygen.

(3.) Colourless *acid fumes* may contain or consist of—

- HCl, recognised by its causing a cloudiness in a drop of silver solution exposed to it.
- HNO_3: addition of *copper* produces red fumes.
- HF: attacks glass; confirmed by repeating experiment in platinum as shown under fluorine.
- SiF_4: dissolves in water with formation of gelatinous *silica* and aqueous SiF_6H_2.

(4.) *Yellowish-green vapours*, bleaching indigo, point to chlorates or hypochlorites.

(5.) *Violet vapours of Iodine* indicate iodides, or iodates present along with reducing agents.

(6.) *Brown vapours* may consist of N_2O_3 (or N_2O_4), indicating *nitrites*, or of *Bromine*, indicating bromides or bromates.

(7.) *Evolution of* CO *or* CO_2, or both, proves the presence of carbon compounds.

Carbonates give CO_2 only
Cyanides } give CO and little or
Formates } no CO_2.
Oxalates give equal vol. of CO and CO_2.
} The mixture does not blacken.

Most non-volatile organic substances (proper) give CO_2, SO_2, and more or less *charcoal.*

513. V. *When heated with* **Oil of Vitriol** *and* **Bichromate of Potash**

all sufficiently non-volatile *carbon-compounds* yield *carbonic acid.*

B.—**For Solutions of Inorganic Metallic Salts.**

(To simplify statements, the solution is supposed to be neutral or alkaline, and to contain no other bases but potash or soda.)

514. I. *On gradual Addition of Excess of Hydrochloric Acid.*

(*a.*) *In the cold, or at a gentle heat,* there may be liberated:
Gaseous CO_2, indicative of Carbonates.
,, H_2S ,, Sulphides.

(*b.*) On boiling (respectively, distillation) there may be liberated (and pass into the distillate):

SO_2, indicative of Sulphites, Thiosulphates, or Polythionates.
NCH, indicative of Cyanides.

The following *insoluble* substances (*inter alia*), may separate out:—

White Sulphur (along with H_2S) from polysulphides.

Yellow Sulphur (along with SO_2) from thiosulphates, polythionates.

Iodine, through the joint presence of iodides and oxidizing, or iodates and reducing, agents.

Silica, a colourless, gelatinous precipitate; can be separated out completely by evaporation to dryness and treatment of residue with water.

Tungstic Acid. The precipitate is white in the cold but becomes yellow on heating.

Molybdic Acid. A white precipitate very readily soluble in excess of acid.

Both these acids are soluble in ammonia; *dry* SiO_2 is not. Solutions of tungstates and molybdates give characteristic colours with zinc and hydrochloric acid.

Stannic Acid, soluble in excess of hydrochloric acid.

Insoluble cyanides; the distillate as a rule contains hydrocyanic acid.

Sulphides of the Arsenic group (as a rule, though not necessarily, along with H_2S), through the presence of thiarsenates, etc.

*Boracic Acid** (from very concentrated solutions only). A crystalline precipitate easily soluble in warm water.

Note.—This list is not complete; on the other hand, as needs hardly be said, the substances named could not by any means be all produced simultaneously; thus H_2S and SO_2, H_2S and I_2, mutually exclude each other.

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* If we had included organic acids, we should here have to add, benzoic or similar acids.

II. *Effect of Reducing Agents.*

515. (A.) Zinc and Hydrochloric Acid act as follows:—

Acid.	*Product.*
Manganese Acids (green or purple solutions).	Manganous salt (colourless).
Chromic Acid (intensely yellow or garnet-red).	Chromic salt (green).
Tungstic Molybdic Vanadic* } Acids; (neutral*) solutions colourless.	Dark-coloured solutions of lower oxides.
Arsenic Acids.	Gaseous AsH_3; little metallic arsenic.
Antimony Acids.	Much metallic antimony; little SbH_3-gas.
Stannic Acid.	Crystalline precipitate of metal.
Nitrogen acids.	Slowly and only partially reduced to ammonia salt.
Phosphorous and Hypophosphorous acids.	(Small quantity of) gaseous PH_3, imparting to the hydrogen the property of burning with a green flame.†
Sulphuric or hyposulphuric acid (in concentrated solutions only).	Small quantity of H_2S.
Other sulphur acids.	Much H_2S.
Iodic acid.	HI.
Bromic acid.	HBr.
Chloric, chlorous, hypochlorous acids.	HCl.
Perchloric acid	is not reduced.

516. (B.) *Action of Zinc and Iron, or of Aluminium, in presence of excess of Alkali.*

Nitrous and nitric acids . . .	on continued heating are completely reduced to ammonia.
Arsenic acids	are slowly reduced to AsH_3.

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† In absence of other hydrides.

517. (C.) *Action of Sulphurous Acid.*

Manganates, permanganates,	reduced to manganous salt.
Chromates	reduced to chromic salt.
Free arsenic acid	on heating very slowly reduced to As_2O_3.
Free iodic acid „ bromic „	reduced, first to halogen, then to HI and HBr respectively.

The acids HClO, $HClO_2$, $HClO_3$, after liberation by sulphuric acid, are reduced to HCl (which precipitates nitrate of silver).

On free *phosphorous* and *hypophosphorous* acids *sulphurous acid* acts as an *oxidizing* agent. When treated with this reagent they yield precipitates of sulphur with formation H_3PO_4.

518. (D.) *Action of Indigo Solution.*

Solutions of nitrates, nitrites, chlorates, hypochlorites, iodates, permanganates, and chromates when mixed with excess of hydrochloric or sulphuric acid, *decolorize* indigo, at least on boiling. Hypochlorites decolorize indigo without the help of free acid; chloric, when liberated by sulphuric, does not bleach indigo in the cold, but it does so on addition of sulphurous acid.

III. *Effect of Oxidizing Agents.*

519. (A.) *Free Chlorine*

converts, in acid as well as alkaline solutions,

Arsenious acid	into arsenic.
Lower phosphorus acids	,, phosphoric.
Lower sulphur acids, except $H_2S_2O_6$	„ sulphuric.

From neutral or acid solutions of

Iodides	Cl_2 liberates I_2, which by an excess of Cl_2 is converted into IO_3H.
Bromides	Cl_2 liberates Br_2, which is not much affected by excess of Cl_2.

520. (B.) *Permanganate of Potash*

offers this great advantage that the reactions are *visible*, in sulphuric solutions through the decolorization of the reagent, in alkaline ones through the separation of a brown precipitate of hydrated binoxide of manganese. By the action of the reagent,

Lower sulphur-acids (except $H_2S_2O_6$), in alkaline as well as acid solutions, are oxidized into *sulphuric*.

Nitrous acid, after having been liberated from a very dilute solution by sulphuric acid, is oxidized into nitric.

Arsenious acid, in acid as well as alkaline solutions, is oxidized into arsenic.

Iodides, in neutral or alkaline solutions, are converted into iodates.

Bromides, under the same circumstances, remain unchanged; but on acidification with nitric acid, a brown precipitate of MnO_2 at once appears.

Dilute Chlorides are not changed. Relatively concentrated solutions of hydrochloric acid, however, decolorize permanganate very appreciably.

Peroxide of hydrogen, in very dilute sulphuric solutions, decolorizes permanganate with evolution of oxygen.

521. (C.) *Iodine Solution.*

(Solution of iodine in iodide of potassium. Such a solution is dark brown; on large dilution with water it becomes yellow.)

Solutions of the acids to be named when rendered alkaline by *alkaline bicarbonate*,* decolorize *iodine*, with formation of iodide and the products to be named.

Arsenites are oxidized into arsenates.
Sulphites „ „ sulphates.
Thiosulphates „ „ tetrathionates.
Hyposulphates are not changed.
Polythianates not $S_4O_6R_2$... ?

These oxidations go on also in acid (HCl)- solutions, but the oxidations are, in general, not complete.

Free *sulphuretted hydrogen* decolorizes iodine with precipitation of sulphur.

522. IV. *Action of Nitrate of Silver.*

This reagent when applied to neutral or alkaline solutions precipitates a great number of acids, but of the silver salts formed only the following are

Insoluble in nitric acid:

Sulphide (black)	Insoluble in ammonia.	
Iodide (yellowish)		
Bromide†	Soluble in ammonia.	†Difficultly soluble.
Chloride		
Iodate		
Bromate		
Cyanide		Decomposed at a red heat; residues, Ag+metal+metallic carbide.
Metallocyanide		

The following, though insoluble in water, are soluble in *nitric acid*:—

Oxide† (brown), carbonate (white), chromate (red), arsenite (yellow), arsenate (brick red), phosphate (yellow), sulphite (white, not very easily soluble in HNO_3). All soluble in ammonia, and more or less readily also in nitrate of ammonia.

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* *Caustic* alkali decolorizes iodine with formation of iodide and iodate.

† Here mentioned because it may be precipitated through the presence of caustic alkali in the original solution.

The following silver salts, when formed in a neutral or alkaline solution, are decomposed, especially on heating :—

Phosphite Hypophosphite	with formation of black metallic silver, and phosphate.
Thiosulphate Polythionates	with formation of black sulphide of silver and H_2SO_4.

If the filtrate from a nitrate of silver precipitate contains chlorine as RClO or $RClO_3$, such chlorine can be precipitated by addition of sulphurous acid (and if necessary H_2SO_4, and more of the reagent), as AgCl.

523. V. *Action of Chloride or Nitrate of Barium.*

By means of these reagents a great number of acids can be precipitated from *neutral* solutions of their salts, but of the baryta-salts which can thus be produced only a few have characteristic properties.

The sulphate [and *selenate*] are the only ones which are not soluble in cold dilute hydrochloric or nitric acid.* The *fluosilicate*, it is true, behaves similarly, but it can easily be distinguished from the other two by its not giving a '*hepar*' when fused on charcoal with carbonate of soda in a reducing flame.† The sulphate is practically insoluble even in hot hydrochloric acid [which decomposes selenate with evolution of chlorine].

[The *tungstate* is white; when decomposed with hydrochloric acid in the heat, it yields a yellow precipitate of tungstic acid.]

The *sulphite* is soluble in hydrochloric acid; the solution decolorizes permanganate with formation of a precipitate of $BaSO_4$.

The *chromate*, pale yellow, somewhat difficultly soluble in hydrochloric acid; zinc and hydrochloric acid convert it into a *green* solution of $BaCl_2$ and Cr_2Cl_6.

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* Observe that $BaCl_2$ and $Ba(NO_3)_2$ themselves are almost insoluble in *strong* HCl and HNO_3.

† SiF_6H_2 is *not* precipated by *strontia*-salts, SO_4H_2 is.

The following acids, *inter alia*, are *not* precipitated by baryta salts, not even from neutral solutions:

Nitric, nitrous, all chlorine acids, bromic acid.*

All lower *sulphur-acids*, except sulphurous. All these, except $H_2S_2O_6$, may by the action of chlorine or permanganate be converted into sulphuric, and thus be recognised as a class.

524. VI. *Action of Magnesia Mixture.*

This reagent, when applied to strongly ammoniacal solutions, precipitates (gradually) *Phosphoric* and *Arsenic* acids only—as $(P\ or\ As)O_4MgNH_4.6H_2O$, white crystalline precipitates, easily soluble in all acids, including acetic, but insoluble in aqueous ammonia. From the hydrochloric solution of a mixed precipitate the arsenic can be removed by means of sulphuretted hydrogen in the heat; from the filtrate the double phosphate is re-precipitated by ammonia.

Note.—Boracic, hydrofluoric, and perchloric acids must be searched for by the application of special operations.

525. Let us now see how far the methods given or suggested in the preceding paragraphs apply to salts of other bases than potash or soda. What was stated under 'I.' with regard to the action of *hydrochloric* acid on potash or soda salts holds fairly well for metallic salts generally; it is only to be observed that, from others than alkaline salts hydrochloric acid may precipitate the insoluble chlorides $AgCl$, Hg_2Cl_2, $PbCl_2$ [$ThCl$]. The formation of these can obviously be avoided by substituting nitric or sulphuric for hydrochloric acid. The methods founded on the insolubility of certain *barium* and *silver*-salts in mineral acids, can in general be safely applied to solutions of *any* salts in the respective acids. The reactions resulting in the formation of barium or silver precipitates insoluble in *water* and in neutral potash or soda salts, may be extended to all those normal salts of the respective acids which dissolve in water; for instance, to the ammonia salts; but just for these they are not quite rigorous, as many of the respective precipitates are more or less largely soluble in certain ammonia salts. Even sulphate of baryta, for instance, is appreciably soluble in nitrate of ammonia.

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* Iodic and periodic acids *are* precipitated by baryta salts.

Magnesia mixture as a test for phosphoric and arsenic acids can be applied to all those substances which are soluble, if not in water, at least in caustic ammonia, or in a mixture of this reagent and sal-ammoniac. It may, for instance, be applied to ammoniacal solutions of the phosphates of cobalt, nickel, or copper, but is not applicable to acid solutions of lime, baryta, strontia, iron, or alumina salts.

In regard to the methods which may be founded upon the reductions and oxidations given in II. and III., we must discriminate between those cases in which the characteristic phenomenon is merely a change in the *reagent* (*e.g.* the decolorization of iodine or permanganate), and those in which that which is seen is the property of a derivative of the acid or class of acids sought for. In the former case negative results, in the latter positive results, can, as a rule, be accepted with perfect confidence.

To point out at least some of the sources of error which have to be guarded against, let us state that *acid permanganate* is decolorized by numerous classes of salts in virtue of their containing certain *bases*, for instance, by ferrous, cuprous, mercurous salts, and that similarly stannous salts, silver salts (among others), have the power of reducing iodine. Indigo solution is decolorized by free chlorine, solutions of ferric chloride, manganic salts, peroxide of hydrogen, and also by certain reducing agents, for instance by hydrosulphurous acid, the lower oxides of vanadium, etc.

526. *Separation of Acids from Bases.*

The following methods may serve for eliminating from a solution such bases as would interfere with the application of certain methods of acid-analysis. Generally speaking, acids may be separated: (1) From the metals of the copper and arsenic groups, by means of sulphuretted hydrogen, when the acids remain dissolved as such. (2) From *lead* and the metals of the *barium group*, by means of sulphuric acid or sulphuric acid and alcohol. (3) From metals of the *iron group*, by means of sulphide of ammonium or sodium. (4) From metals *forming insoluble carbonates*, by treatment in the heat with excess of carbonate of potash or soda. (5) From metals forming oxides or hydrates insoluble in *caustic potash or soda*, by means of *these* reagents.

Notes.—None of these methods are sure to apply to *cyanides;* apart from these, (1) and (2) are almost generally applicable, but unfortunately many acids, for instance iodic, chromic, sulphurous, are decomposed by sulphuretted hydrogen. *Regarding* (3), (4), *and* (5).—Do not apply to phosphate of alumina. In all cases the precipitates are liable to retain more or less of the acids as basic salts. (4) does not apply to phosphates of Al_2O_3, Fe_2O_3, BaO, SrO, CaO, MgO. (4) and (5) are inapplicable to the compounds of ferric, aluminic, and chromic oxides with non-volatile organic acids. These are only the more important of the qualifications which the methods are liable to. In all cases we must take care to remember that the acids extracted may *not* have pre-existed in the substance.

IV.—ANALYSIS OF SUBSTANCES OF UNKNOWN NATURE.

527. To be able to lay down even a provisional scheme for the analysis of a substance, it is obviously necessary to know something about its chemical nature. If this indispensable basis for a systematic method is not given by the known history of the substance under examination, try to obtain it by a judiciously conducted series of preliminary observations and experiments. Regarding the manner in which such pioneering work should be conducted, it is not possible to give definite directions. Hence, if in what now follows we occasionally assume the imperative mood, the student must understand that we do so only for the sake of shortness and conciseness of expression; what we really mean to give is no more than a stock of information from which it is left to his ingenuity to select what applies to the case in hand, and which he will not unfrequently have to supplement by methods of his own invention.

For the sake of simplicity we assume the substance under investigation to be a solid, although some of what will have to be said will be seen to be independent of this supposition.

The domain of analysis commences where the resources of mechanical modes of separation end; hence, if an obvious mixture or juxtaposition of different things should present itself for examination, we naturally separate these, if practicable, from one another, and examine each of them for itself. As a rule, it is expedient to begin with an

528. *Examination into the physical properties of the Substance.*

1. We see whether the substance is apparently *homogeneous* or not, using a microscope if this appears necessary or expedient.

2. We ascertain whether it is amorphous or crystalline, and in the latter case take note at least of the habitus, if not the exact form, of the crystals.

3. We notice the behaviour of the substance to light; *i.e.* its degree of transparency, its lustre, its colour in transmitted and in reflected light, etc.

4. We notice its state of *cohesion*, *i.e.* its degree of hardness, plasticity or brittleness, etc.

5. We observe its density, at least by guessing; sometimes an exact determination of the specific gravity gives useful hints.

6. In some cases it will be found expedient to see if the substance (or perhaps part of it) is attracted by a *magnet*. If it is, this points to the presence of metallic iron, nickel, cobalt, or magnetic oxide of iron.

7. We study the behaviour of the substance when successively exposed to higher and higher temperatures. This however generally leads to chemical changes; we therefore reserve the discussion of this point for the following chapter.

Note.—The exact observation of the physical properties of a substance, when backed by a sufficient knowledge of descriptive chemistry, often enables one to at once identify it with a certain chemical species, or as belonging to this or that genus of compounds.

Metals and alloys, as a class, can generally be recognised by their physical properties. It must however not be forgotten, that there are many minerals (for instance galena, plumbago, the several pyrites) which have the *appearance* of, and yet are not, metals, while on the other hand, many metals, when given in a fine state of division, are devoid of metallic lustre. (Exx.: precipitated antimony, iron reduced by hydrogen, platinum black.)

Preliminary Chemical Examination.

529. If the physical properties of our substance do not happen to point so decidedly to a certain chemical individual, or class of individuals, as at once to give to the chemical investigation a certain special direction, we now try, by a series of tentative chemical experiments, to obtain the data for the framing of a systematic process of analysis.

In reviewing for this purpose the several analytical methods given in the preceding sections of this book, we find that they are all either methods for the detection of certain salt radicles or methods of ultimate analysis pure and simple, and that, in either case, they all start, either by treating the substance at a high temperature with dry reagents, or by subjecting it to the action of liquid disintegrators, such as water or mineral acids. Hence, in the examination of a substance of unknown nature, it is obviously expedient to begin by studying, at least in a cursory manner, its behaviour at high temperatures, and its comportment with the menstrua named.

Should it turn out that the substance is, either by the application of heat, or of menstrua, clearly separable into two or more different parts, it is generally advisable to effect a separation in a sufficiently large scale, and to examine each of the products for itself.

In any case these preparatory studies will enable us to see to which of our methods of testing the substance is directly accessible. Regarding the mode of discounting these methods, we have the choice between two principles: we may either start with certain *hypotheses* regarding the composition of the substance, and by properly devised methods test for the constituents presumed to be present. Or else we may take as independent variables a series of *operations*, known to be capable of extracting answers from *as great* as possible variety of bodies, apply these operations one after the other, and collect the results as they come out. A little meditation will show that, with a substance of unknown nature, the second plan is to be preferred, at the outset at least. As soon, of course, as some knowledge of the composition has been gained, it may be expedient to adopt the first method of investigation.

In the following chapters we give an exposition of such operations as are likely, when applied to a substance, to extract valuable answers.

DRY-WAY TESTS.

A.—*Such in which the Substance is heated indirectly.*

530. I. **Effect of Heat alone.**—Heat a small quantity of the substance in a *sublimation tube*, first gently, then more and more strongly, until the glass becomes inconveniently soft, and observe what takes place, *i.e.* if, respectively at what temperature, the substance *fuses*, if it is (totally or partially) volatilized, if there is a marked change of colour, etc. etc.

Many *organic substances* will be decomposed with elimination of charcoal. If charcoal is formed, incinerate a separate portion of the substance in a porcelain dish and keep the ash for other dry-way tests.

Some classes of compounds (*e.g.* nitrates, chlorates, oxides of silver or mercury) will give off *oxygen*. Many unstable *carbonates* give off carbonic acid; *acid sulphites*, and *hyposulphates*, will give off sulphurous acid.

Of the great variety of *Sublimates* which may present themselves, the following are comparatively easy of identification:—

Water or aqueous solutions of *ammonia*, or of volatile acids.

Mercury, *Arsenicum*, *Cadmium*.

Arsenious oxide As_2O_3: colourless, sparkling crystals, readily volatile far below redness.

Antimonious oxide Sb_2O_3: white, crystalline; far less volatile than As_2O_3; when heated in *air*, gradually changed into amorphous non-volatile Sb_2O_4.

Tellurious oxide Te_2O_3: similar in appearance to Sb_2O_3, but perfectly non-volatile; fusible into colourless drops.

Iodine: plumbago-like, crystalline; forms violet vapours.

[*Selenium*]: in thin layers red; in crusts, black.

Certain sulphides, e.g. As_2S_3, HgS.

A sublimate of HgS forms a black mirror, very similar in appearance to one of arsenicum; the two substances are distinguished by their comportment when heated *in air*. As is converted into As_2O_3; HgS into a sublimate of Hg-globules and SO_2-gas.

Haloids of mercury.—HgCl, $HgCl_2$, HgBr, $HgBr_2$: white or whitish crusts; HgI_2: yellow crystals, which when rubbed with a glass rod become crimson.

Ammonium salts: white crystalline crusts, soluble in water.

531. II. Effect of Heat and Atmospheric Oxygen.—Heat a small fragment of the substance in a '*draught-tube*,' taking care, by holding the tube slantingly, to produce a current of air. Many substances will undergo oxidation and yield characteristic products.

Sulphur, most metallic sulphides, and certain other sulphur compounds, yield sulphurous acid, recognised by its smell and acid reaction. Part of the liberated sulphur may escape oxidation.

[*Selenium* and *Selenides*] behave similarly; only free selenium more frequently than free sulphur appears as a sublimate.

Arsenic and many Arsenides yield sublimates of As_2O_3.

Antimony, its sulphides and some metallic antimonides, yield sublimates of Sb_2O_3.

Tellurious oxide, *molybdic oxide* MoO_3, *stannic oxide* (formed by oxidation of volatile SnS_2) will occasionally present themselves as sublimates.

532. III. **Effect of Heat and Reagents.**— (a) *Bisulphate of potash.* Some classes of compounds when heated with this reagent in sublimation tubes yield characteristic volatile products; for instance:

Fluorides yield vapours of HF, attacking glass.

Nitrates, *Nitrites*: brown fumes of N_2O_4.

Bromides: brown fumes of bromine.

Iodides: violet vapours of iodine.

Compare chapter on action of *Oil of Vitriol* on salts; § 512.

(b) *Soda-Lime.*—Compounds containing nitrogen in direct combination with hydrogen or metals or carbon, when heated in a sublimation tube with this reagent (and nitrates, nitrites, and other NO_2-derivatives, when heated with the reagent and combustible matter) yield *Ammonia.*

(c) *Caustic Soda and Nitrate of Potash.*—Many substances when fused (in a silver dish) with these reagents, yield characteristic products of oxidation. Thus, for instance, compounds of *chromium*, [vanadium,] *manganese*, *tungsten*, *molybdenum*, *sulphur*, *phosphorus*, yield alkali salts of:

CrO_3 $[Va_2O_5]$ MnO_3 WoO_3 MoO_3 SO_3 P_2O_5*

The colours of the fused masses are:

yellow o Intensely green o o o o

The salts are all soluble in water. For reactions of the solutions, see §§ 187, 189.

B.—*Operations in which the Substance is heated directly in the Flame.* (*'Flame Tests.'*)

533. In performing these tests we may either avail ourselves of a *blowpipe-flame*, or else, following the directions of

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* *Ortho*-phosphoric acid.

Bunsen, use the non-luminous flame produced by the combustion of a mixture of coal-gas and air (the flame of a *Bunsen's lamp*).

How to produce a *blowpipe flame*, and also the difference between a '*reducing*' and an '*oxidizing*' flame, were fully explained in I., Exercises X. XI. XII.

If we wish to adopt *Bunsen's* modus operandi, we must first of all procure a good '*Bunsen's lamp*,' which should be provided with a slide at the draught-holes to regulate the draught, and with a conical chimney to steady the flame, and be constructed so that, supposing the draught-holes to be wide open, it gives a perfectly non-luminous flame with the particular kind of coal-gas which is used in the laboratory. In such a flame, we easily distinguish two parts, viz.: 1st, the '*dark cone*' containing the relatively cold mixture of gas and air; 2d, the '*flame-mantle*' surrounding and surmounting the dark cone, which consists of the burning mixture of gas and air. It is the *mantle* which is used as a heating medium. The *highest* temperature prevails in the centre of the '*zone of fusion*,' *i.e.* that zone of the annular part of the mantle which lies at about ¾th of the height of the '*cone*.' The inner surface of this zone (the '*lower reducing region*') has reducing, the outer surface (the '*lower oxidizing region*') has oxidizing, properties. These two regions can in general be looked upon as being equivalent in their actions to a reducing and an oxidizing blowpipe-flame respectively. This, however, does not quite hold for the reducing region, which, containing a comparatively large amount of free oxygen besides unburnt hydrocarbons, fails to effect certain reductions which succeed in a reducing blowpipe-flame. The apex of the mantle, being of a relatively low temperature and rich in oxygen, is adapted chiefly for *roasting operations*. By partially closing the draught-holes, it is easy to produce near the upper end of the flame a *luminous tip*, which, although it contains a considerable quantity of unburnt hydrocarbons, will *not* deposit any soot on a cold porcelain basin held in it. It is such a tip which must be used for the execution of Bunsen's '*film-tests*' (*vide* infra). These film-tests cannot be conveniently executed with a blowpipe-flame; in case of any of the rest of the flame-tests to be described, however, it is, in general, more a matter of taste than anything else whether we prefer the older or the newer modus.

534. *Behaviour of Substances when heated in the flame by themselves.*

As a means for studying the comportment of a substance at high temperatures, the blowpipe offers the advantage of being the more powerful source of heat, while the Bunsen's lamp, on the other hand, enables one to work under more definite conditions, and also has this in favour of it, that it leaves both hands free for operating. To utilize the possibility however of producing by means of a Bunsen's lamp the same heat-effects as those attainable in a blowpipe-flame, we must take care to avoid all unnecessary loss of heat by radiation and conduction. We accordingly work upon *very small* samples, and use as supports for these either very thin platinum wire (1 decimeter should weigh at most 34 milligrammes), or, for substances attacking, or refusing to adhere to, platinum, fibres of dense asbestos about ½ mm. thick. To form an idea of the temperature attained in a given case, we may judge by the kind of light which is emitted by a thin platinum wire exposed to it, but we must not draw conclusions from the light emitted by the substance. *Bunsen* distinguishes the following six grades: (1) below redness; (2) commencing red heat; (3) red heat; (4) commencing white heat; (5) white heat; (6) strong white heat. The degree of *fusibility* of a substance may be determined by exposing it successively to the six temperatures and noting the effects. To define the *volatility* of a substance (if it is at all volatile in a gas-flame) we may compare the time required for the volatilization of, say, one centigramme of substance, and compare it with that required, under the same circumstances, by the same weight of *chloride of sodium* or other standard substance.

Infusible bodies, when exposed to the hottest part of the flame, usually emit intense light. Such is the case, for instance, with lime, magnesia, pure silica, alumina. Erbia has the exceptional property of emitting coloured light.

535. Flame colouration.—Many substances, when gradually volatilized in a Bunsen's flame, impart, or yield products of dissociation imparting, to the flame characteristic colours. This holds especially for the compounds of certain metals, and in the case of these, it is as a rule the *metal* which determines the nature of the light emitted. If a metallic compound gives no colour when exposed to the flame, it will frequently do so after having been first heated in a reducing flame, and subsequently moistened with hydrochloric acid, the metal being by this operation changed into a volatile chloride. Many alkaliferous silicates yield the flame-colours characteristic of their alkali-metals only after having been mixed with *sulphate of lime.*

A *crimson* colour points to the presence of lithium or strontium.

A *reddish* colour indicates	calcium.
A *bright yellow* colour	sodium.
A *yellowish-green* colour	barium.
A pure *green* colour	thallium (or iodide of copper).
A *bluish-green* colour	chloride or bromide of copper.
A *pure indigo blue*	indium.
A *violet* colour	potassium [or rubidium, or cæsium].

In the case of a mixture of several metals we can sometimes observe the different colours successively, in consequence of the respective compounds possessing different degrees of volatility and passing into vapour one after the other.

However, the mere *observation* of the colour of a flame, as a rule, is not sufficient for obtaining definite results. Perfect certainty can be obtained only by *analysing* the colour by means of a *spectroscope.*

With regard to the construction of this instrument, we refer the student to the handbooks of Physics. To enable one to interpret its indications, all that it is necessary to know is, that, assuming it to be directed to a coloured flame, and properly adjusted, it presents to the observer as many images of the slit as there are refrangibilities in the light which passes through the slit. Hence, a flame emitting, say, yellow light, red light, and violet light (of the definite refrangibilities y, r, v respectively) will give a spectrum consisting of three images of the slit, viz. a yellow one, a red one, and a violet one.

The spectra of glowing vapours of metallic compounds, as produced by means of a Bunsen's lamp, usually consist of a discontinuous series of lines or bands, the mutual positions of which depend on the nature of the vapour, but are independent of the fluctuations of temperature which such a flame is liable to.

Some of the spectra, for instance those of the alkali-metals, are so simple and characteristic, that they are easily recognised by ordinary inspection; but even in the case of these it is better, and with complex spectra it is necessary, to identify the several lines or bands supposed to be owing to the presence of this or that element, by proving their exact coincidence with the corresponding lines or bands as produced from a standard substance of undoubted identity and purity.

Two contrivances are used for this purpose. Either the spectroscope is provided with a figured scale and optical arrangements, constructed so that the image of the scale, as seen by the observer, runs along the spectrum, and each of its marks always corresponds to the same refrangibility; or else the instrument is provided with a reflexion-prism placed before the slit in such a position that it covers one half of the slit, and that the rays of a flame placed opposite to it are reflected into the tube in the direction of its axis.

It is easily seen that if we place two flames emitting the same kind of light, the one opposite the slit, the other opposite the reflexion-prism, the two spectra will run alongside of each other so that the bands of the one correspond exactly with those of the other.

336. *Bunsen's Film-Tests.*

The *oxides* of certain *volatile metals* (and such other compounds of these metals as are, by the action of the gases of the flame, converted into oxides), when exposed to the '*luminous tip*' of a Bunsen's flame, are reduced, with formation of vapour of metal, which, in passing through the flame into the air, generally gets re-oxidized. To collect the *metal* as such, *i.e.* in the form of a '***Metallic Film,***' hold a Berlin basin of 1 or 2 decimeters diameter (which must be glazed outside) close above the sample. The metal will condense on the porcelain, forming a dark-coloured deposit. If it is desired to collect larger quantities of the metal, the basin must be charged with water, previous to its being used, so as to keep the condensing surface cold. Or, what is sometimes preferable, we use, instead of the basin, a large test-tube half full of water and containing a few bits of marble to keep the water from 'bumping.' The metals which can be reduced in this manner may be divided into three classes according to their comportment when moistened in the cold with *nitric acid* containing 20 p.c. of N_2O_5.

I.	II.	III.
Scarcely attacked.	Very slowly dissolved.	Instantly dissolved.
Arsenic, Antimony, Tellurium, Selenium.	Bismuth, Mercury, Thallium.	Lead, Cadmium, Zinc, Indium.

To produce an Oxide Film.—Hold the basin in the upper oxidizing region, after having previously lowered and lessened the flame so that the oxide does not get diffused over too large a surface. The oxide-films may be examined by noting the effects produced: (1) by a solution of stannous chloride; (2) the same reagent and excess of caustic soda; (3) ammoniacal nitrate of silver. The silver solution is spread over the film by means of a glass rod, and the moist film then exposed to a current of air previously passed through a strong solution of ammonia. (4) The *oxide* film may be changed into an *iodide*-film by exposure to fumes of hydriodic acid, *i.e.* by holding it over a bottle containing moist iodide of phosphorus. The iodide film may then be examined (1) by *breathing* on it, soluble iodides will become invisible; (2) by exposing it to a current of *ammoniacal* air; (3) by exposing it to a current of air saturated with *sulphide of ammonium*, and thus converting it into sulphide.

The following table, extracted from a more elaborate one appended to *Bunsen's* paper, will enable the student to interpret his observations.

537. TABLE ON FILM TESTS

for Arsenic, Antimony, Tellurium, Selenium, Bismuth, Mercury, Thallium, Lead, Cadmium, Zinc.

The Metallic Deposits

usually consist of two parts, viz., a continuous '*film*' and a discontinuous '*dust*' scattered over the porcelain surface.

	All the Elements named except Se and Hg.	**Selenium.**	**Mercury.**
Colour of Film	Black	Cherry-red	Grey deposit which when scraped together unites into liquid globules.
,, Dust	Brown	Brick-red	

[illegible]

[illegible] visible on the [illegible] PbO. CdO. which are [illegible] respectively.

[illegible] Characteristic Reactions with [illegible]

	[illegible]	[illegible]	[illegible]
[illegible]	brick-red.	Black.	White.
[illegible]	Black.	Black.	Black.

Ammoniacal Nitrate of Silver

when applied (as explained above) to oxides of *arsenic*, produces an *egg-yellow* or *brick-red* colour; with *antimony-oxide* it yields *black* suboxide of silver.

Properties of the Iodide-Films of

		Te	**Sb**	**As**	**Se**	**Hg***	**Pb**	**Th**	**Bi**
	Colour.	Brown.	Orange.	Egg-yellow.	Brown.	Red or yellow.	Egg-yellow to lemon-yellow.	Lemon-yellow.	Bluish brown, dust red.
The Iodides and:	*Moisture.* †	Colour vanishes, but reappears after some time.			Vanishes partly.	Colour permanent.			Vanishes, to reappear.
	Ammonia †	Colour permanently destroyed.			Permanent.	Vanishes, but reappears afterwards.		Permanent.	Becomes red or yellow: when dry, brown.

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* Produced from metal by exposure to iodine-vapour.

† See end of § 140.

Flame tests in which the Substance is heated along with Reagents.

538. (1.) **Cobalt Nitrate.**

Certain white infusible oxides when moistened with cobalt-solution and then strongly heated in the oxidizing flame on charcoal (or an asbestos-stick), assume characteristic colours (without fusing).

Product from :	Al_2O_3	MgO	ZnO	SnO_2
is	blue.	reddish.	green.	bluish-green.

The colours are distinctly visible only after cooling.

Compare §§ on the respective metals.

(2.) **Carbonate of Soda.**

539. (a) *On Platinum wire.*

Silicic acid and highly acid silicates when fused with carbonate of soda dissolve with evolution of CO_2 and formation of a bead, which, if *sufficiently rich in silica*, remains clear on cooling.

Chromium- and *Manganese*-compounds, when fused with soda in the oxidizing flame, give characteristically coloured beads. (Cr. yellow; Mn. green.) Comp. §§ 187, 536.

540. (b) *On Charcoal.*

Many substances when heated to redness with charcoal or carburetted hydrogens undergo *reduction*, and not unfrequently the properties of the reduction products allow one to draw conclusions regarding the elementary composition of the substance.

The *modus operandi* may assume one or other of the following two forms :—

(1.) (*Old Style.*)—The finely powdered substance is placed on the palm of the left hand along with 2 or 3 times its bulk of carbonate of soda, and the two substances are mixed by means of an ivory or steel knife-blade, which must from time to time be moistened with saliva so that the mixture ultimately forms a rather dry paste. This paste is placed in a small hole made in the *smooth* surface of a piece of *good** charcoal and heated in the reducing blowpipe flame, first gently, and then more and more strongly until the desired end is obtained.

(2.) *Bunsen's modus.*—An ordinary lucifer match (minus the head) is rubbed over with fused carbonate of soda crystal, and then charred in a flame so as to be converted into a rod of charcoal soaked with carbonate of soda.

A very small portion of the substance to be operated upon is then placed on one end of the charcoal-stick and exposed to the '*lower reducing region*' of a Bunsen's flame.

Compounds of sulphur [selenium, tellurium] when operated upon as just described, yield '*hepars*,' *i.e.* fluxes containing Na_2S, [Na_2Se, Na_2Te], and consequently when placed on a silver coin and moistened with water, produce *black stains*. *Many metals*, by the same operation, can be reduced from their oxides or salts, and are obtained either in the shape of directly visible *beads* or in the shape of fine particles diffused through the flux and charcoal. How in the latter case the metal can be obtained for itself by elutriation, has already been explained in Exercise X.

If the metal is volatile from under a flux at the temperature employed, part of it at least will be converted into a vapour which, in passing through the flame, is burned into oxide; and, if the operation is performed on a *block* of charcoal, part of the oxide will be deposited on the charcoal as an '*oxide-film*.' We now proceed to state the behaviour of the several individual metals.

Mercury, arsenic, zinc, cadmium are completely volatilized.

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* The charcoal should be made of fir-wood or poplar-wood. It must be free from discontinuities, very light, poor in ash and completely burnt out, so as not to crackle or give off fumes on heating. The charcoal should be cut into square blocks by means of a saw, in such a manner that two of the faces when produced would go through the axis of the branch or trunk. These faces (on which the year-rings appear as a set of parallel straight strips) are best adapted for blowpipe-work. *Excellent* blowpipe-charcoal can be procured from Freiberg in Saxony.

Of the arsenic a part *may* be deposited on the charcoal as As_2O_3; zinc and cadmium yield considerable oxide-films, which can be recognised, the CdO by its brown colour, the ZnO by its behaviour to *cobalt-solution.*

The following metals are easily obtained as very readily fusible beads:

Bismuth.	Lead.	Antimony.	Tin.
Brittle.	Ductile.	Brittle.	Ductile.
Yellow oxide-film.		Copious white crystalline deposit of oxide.	Little or no oxide.

The following metals, being rather difficultly fusible, will, as a rule, form no beads, but have to be searched for in the flux:

Silver.	Copper.	Gold.
White.	Reddish.	Yellow.
No oxide-film.		
Soluble in nitric acid.		Insoluble in HNO_3.

The following metals, *being infusible* and non-volatile, are obtained, by elutriation, as heavy powders showing no signs or only feeble† signs of incipient fusion:

Iron.	Nickel.† Cobalt.†	Platinum.	Palladium.
Magnetic.		Insoluble in nitric acid.	Soluble in nitric acid.
Easily	Difficultly		
soluble in hydrochloric acid.			
Readily dissolved by nitric.			

It needs hardly be said that the properties of a metal may be considerably modified by the presence of impurities, not to speak of admixtures. In presence of *arsenic*, most of the metals will be obtained as arsenides which differ considerably from the metals themselves in their properties. Thus, for instance, the arsenides of iron, cobalt, nickel, and platinum, are easily fusible.

541. (3.) Borax and Microcosmic Salt.

Regarding the rationale of these tests we have nothing to add to what has already been explained in Exercise XII. except the statement that microcosmic salt, when heated by itself as long as volatile matter goes off, leaves a residue of $Na_2OP_2O_5$ which resembles and behaves to metalled oxides pretty much like fused borax. If the tests have to be executed with Bunsen's flame, we must take care to use very thin wires and very small beads.

In using microcosmic salt or borax for the detection of metals we must not lose sight of the fact that it is only the oxides of the metals which produce the characteristic phenomena, and that consequently the tests apply to *salts* only in so far as these are, by the action of the gases of the flame, converted into oxides, without formation of inconvenient bye-products. Sulphides should never be used as such, but first, by roasting, be converted into oxides.

The following table gives the most important of the tests under consideration. h. stands for hot; c. for cold; 'sat.' for richly charged with the respective oxide.

	OXIDIZING FLAME.		REDUCING FLAME.	
	Borax.	**Microcosm. Slt.**	**Borax.**	**Microcosm. Slt.**
Cobalt.	Blue bead.		Blue bead.	
Nickel.	h. Reddish. c. Much fainter. sat. Brown.	h. Brown or brownish yellow. c. Much fainter. In presence of Co : green.	Grey and turbid from metal, which gradually agglomerates, leaving a clear bead.	Same as in oxidizing flame.
Manganese.	Intensely amethyst-red.	Same colour, but less intense.	Colourless.	
Copper.	h. Green. c. Blue.	Same as borax, but less intense.	Brown-red and opaque.	Same as borax. Sometimes : h. Colourless. c. Transparent red.
Chromium.	Emerald-green.		Emerald-green.	
Iron.	h. Yellow. c. Colourless. sat. : h. Red ; c. Yellow.	h. Yellowish-red. On cooling green. c. Colourless.	Bottle-green.	sat. h. Red. sat. c. Reddish. Small quantities produce no colour.
Uranium.	Yellow.	h. Clear yellow. c. Yellowish green.	Green.	Green.
Molybdenum.	h. Yellow. c. Almost colourless.	h. Greenish. c. Almost colourless.	Dark brown. sat. Brown flakes of MoO_2.	h. Dark green. c. Less intense, but purer.
Tungsten.	Colourless.	Colourless.	Yellow.	Blue. In presence of iron : blood-red.
Titanium.	Colourless.	h. Yellow. c. Colourless.	First yellow ; on continued heating dark blue.	c. Violet ; in presence of iron : blood-red. h. Yellowish.
Silica.	Colourless bead. sat. Opaque.	Does not dissolve. Splinters of silicates yield SiO^2-skeleton.	As in oxidizing flame.	

542. *Preliminary Wet-Way Tests.*

In our introductory remarks on the preliminary chemical investigation of a substance (§ 333) we already took occasion to say that it was expedient, at the very first stage of this part of the work, to study, at least in a tentative way, the comportment of the substance with water and with the ordinary mineral acids. Of other general operations, the following may be mentioned as being likely to extract valuable answers :

(1) Treatment of the substance with *oil of vitriol* in the heat. (For interpretation of phenomena see § 516.)
(2) Application of the same reagent along with *bichromate of potash* (§ 517). (3) Examination of the substance with *zinc and hydrochloric acid* (to test for tungstic, vanadic, molybdic, chromic acid). Of the infinite variety of *specific* questions which, at this stage of the analysis, it *may* be expedient to address to a substance by wet-way operations, we can of course take no notice here. But it is perhaps as well on this occasion to remind the student that the object of the preliminary investigation of a substance must be to try and achieve one of the three things, viz., either to identify the substance with a definite chemical species, or to prove it to consist of members of one or the other of those particular classes of compounds for which we possess, so to say, ready-made methods of analysis, or, if this also fails, to see our way to such a method of disintegration, as will bring at least the *metallic* elements present within the range of the ordinary systematic methods of separation so that, supposing the metals to be all detected, we have a secure basis for the exhaustive detection of the non-metallic constituents.

METHODS OF DISINTEGRATION FOR SOME OF THE MORE FREQUENTLY OCCURRING CLASSES OF SUBSTANCES.

543. I. *Metals and Metallic Alloys.*

A substance which presents the physical and mechanical characters of a metal, and which, when heated in a draught tube, does *not* (like certain metallic-looking sulphides) give off sulphurous acid, can in general be looked upon as belonging to this class, and consequently be assumed to contain no non-metallic elements, except perhaps small quantities of carbon, silicon, sulphur, phosphorus, nitrogen. There is no *direct* qualitative method for identifying *as metals* such metallic substances, which like platinum black, precipitated antimony, etc., are apparently devoid of metallic properties.

In examining an *alloy* we first try in a preliminary manner the action of water and of hydrochloric acid. If neither of these two reagents acts energetically it is, as a rule, best to use as a disintegrant:

Nitric Acid.—The finely divided alloy is treated first with acid of 1·2 spec. grav., which, if its action is not sufficiently quick, may be strengthened by subsequent addition of acid of 1·4 spec. grav. When the metal is completely disintegrated, the mixture is evaporated to a small bulk to expel the greater part of the excess of acid, the residue mixed with water and, if necessary, filtered. The *residue* may contain : (1) *gold*, *platinum* (and certain other metals of the platinum-group) as such; (2) *antimony*, *tin* as oxides or arsenates; (3) *bismuth* as arsenate or phosphate. Platinum and gold (when free from (2) or (3)) are easily recognised by their high specific gravity and their dark colour, and, after conversion into chlorides by treatment with aqua regia, can be detected side by side of another. To effect a rough analysis of the complex (2)+(3), treat the oxides with pure *zinc and hydrochloric* *acid*[*] until they are completely reduced, and next extract, first the excess of zinc and then the tin, by repeated treatment with boiling hydrochloric acid. Digest the residue with excess of yellow sulphide of ammonium; the bismuth remains as sulphide, the antimony passes into solution as a thiosalt which, on evaporation to dryness, leaves the antimony in the form of a brick-red sulphide readily soluble in strong hydrochloric acid in the cold. A more exact method would probably be, to at once convert the oxides into sulphides by treatment with yellow sulphide of ammonium; the bismuth would remain as sulphide, the antimony, tin, arsenic, would pass into solution as thiosalts, and could be precipitated therefrom by hydrochloric acid as sulphides. The phosphoric acid, if present, would pass into the filtrate. The *nitric solution* cannot contain any tin, nor more than traces of gold or antimony, and it may, in general, be assumed to be free of platinum, but it may contain any of the other metals; arsenic as oxide, the rest as nitrates. Its analysis presents no difficulties. In the treatment of an alloy with nitric acid the *sulphur*, if present, gets converted into sulphuric acid; the *phosphorus* into orthophosphoric; the *carbon and silicon* partly into the elementary form, partly into the oxides CO_2 and SiO_2.

Alloys which are not attacked by nitric acid must be treated in the heat with strong hydrochloric acid, with gradual addition of nitric acid, the former acid being kept in excess, so that the metals are ultimately present as chlorides. If the *bulk* of the excess of acid is removed by evaporation, and water added, the silver only remains undissolved, while all the other metals pass into solution. From the solution it is always best, first to remove the gold and platinum by means of hydrogen, formate of soda, or other specific precipitants (see §§ 73, 76, 106), and then to search for the rest of the metals in the usual manner.

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[*] *If* arsenic is present, part of it will go off as AsH_3, which may be collected in $AgNO_3$-solution.

Alloys acting strongly upon water should be repeatedly treated with this liquid in the heat as long as there is any perceptible action,* and the aqueous extract be examined by itself for what may be present in it (*i.e.* for K, Na, Ba, and metals soluble in caustic alkali, *e.g.* Al, Zn). The residue is analysed by means of nitric acid as shown above. The same holds, *mutatis mutandis*, for

Alloys acting strongly upon hydrochloric acid.—The hydrochloric solution is not likely to contain any metals of the copper and arsenic groups except tin and cadmium. The '*hydrogen*' evolved may contain hydrides of arsenic, antimony, phosphorus, sulphur; to detect these constituents, pass the gas, first through a tube full of crystals of sulphate of soda, to absorb the HCl, and then through nitrate of silver; the elements named are converted into respectively Ag_2S, Ag_3PO_4, $SbAg_3$ (precipitates), and As_2O_3 (solution), and in these forms may be identified.

To test a metal or alloy for *nitrogen*, fuse it with caustic alkali; the nitrogen goes off as ammonia. Compare § 382.

II. *Sulphides.* III. *Haloids.* IV. *Fluorides.* V. *Phosphates.* VI. *Silicates.*

544. If the substance under investigation, either from its known history, or by the results of the preliminary examination, should be proved to consist, substantially at least, of constituents of any *one* of these classes, we naturally apply the special methods of analysis which were given in Part III. under the respective elements; taking care, however, to keep alive to the possible presence of foreign admixtures, which, if they should present themselves, must be disposed of by supplementary operations.

545. VII. *Inorganic Substances generally.*

This heading is meant to cover all those cases in which the preliminary investigation of the substance has brought out nothing but the negative fact that it is free from combustible carbon compounds.* In such a case the course generally adopted is to start on the supposition of the substance being a mixture of the following classes of compounds:

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* The hydrogen evolved may contain AsH_3.

(1.) Salts, soluble in *water* and substances which by treatment with water are converted into solutions of salts (Exx.: NaCl, PCl_5).

(2.) Compounds which, though insoluble in water, can be converted into aqueous salt-solutions by means of:

(*a*) Dilute or strong *Hydrochloric Acid* or **Dilute** *nitric acid*, acting by double decomposition (Exx.: $CaCO_3$, CdS).

(*b*) *Strong Nitric Acid* of 1·4 or 1·5 sp. gr., or

(*b*)^1 *Aqua Regia*, acting as **oxidizing agents.**

(3.) Compounds which, in a practical sense at least, are proof against all these disintegrants.

The method in its general form accordingly consists in this, that by successively applying to one and the same specimen of the substance the appropriate disintegrants, we try to extract from it and collect in *separate solutions* what belongs to class (1.), class (2.)*a*, class (2.)*b*, and class (2.)*b*^{1} respectively. Whether in proceeding to extract from it the constituents (2.)*a*, we should employ one or the other of the acids named, must be decided by tentative experiments or small specimens of the residue left after treatment with water. *Nitric acid*, in lieu of hydrochloric, should be used only, when the latter, through the presence of mercurous oxide or silver, would produce insoluble chlorides. Preliminary trials also must decide whether or not, in a given case, it is at all worth while to discriminate between any two successive groups. There is in fact no sharp line of demarcation between any two of these groups. Thus, for instance, sulphate of lime stands between (1.) and (2.)*a* ; sulphide of copper or nickel belongs to both (2.)*a* and (2.)*b*. It is also easily seen that a substance, which by itself is insoluble in hydrochloric acid, may pass into the hydrochloric solution in consequence of the presence in the substance of oxidizing agents. Hence, although the successive application of two menstrua may divide a substance into two portions, it does not follow that it has effected a real separation in the specific sense. Such sham separations we must of course try as far as possible to avoid executing.

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* We also assume, for simplicity's sake, fluorides to be absent. On the other hand, the instructions to be given may be assumed to include *cyanides* decomposible by acids.

With regard to the practical working of the process we must confine ourselves to saying that the substance, before being attacked by any disintegrants, should be *powdered* (the more finely the harder and denser it is), that the several menstrua must, as a rule, be applied in the heat, and that, supposing an acid to have done its work, the mixture must first be evaporated* to expel the bulk of the acid, and then diluted with water before the residue left is separated by filtration.

In treating a substance with *acids* we must take note of the phenomena going on. In the treatment of a substance with *hydrochloric acid* there may be liberated,

(1.) *As gases or vapours :—*

CO_2 . . . indicating carbonates.
SO_2 . . . " sulphites or polythionates.
H_2S . . . " sulphides.
NCH . . " cyanides.
Cl_2 . . . " peroxides, etc.

And there may be formed:

(2.) Precipitates of sulphur, sulphides, chlorides (AgCl, Hg_2Cl_2), silica, tungstic acid,† etc. etc.

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* Such evaporation should, strictly speaking, be always done in a retort connected with a condenser, and the distillate be examined for volatile substances, such as HNC, etc.

† For further information see § 514.

The action of *nitric acid* or *aqua regia* may cause the formation of precipitates of sulphur, insoluble sulphates, chloride of silver, etc. etc.

Hence the *residue* left after treatment of a substance with water and acids, may contain a variety of things besides what was originally present of compounds of class (3.) The following is a list of the more frequently occurring substances, and gives hints as to the modes to be adopted for their identification or disintegration.

546. *Sulphur.*—Easily recognised by its fusibility and ready combustibility into SO_2. A residue left after combustion consists generally of some sulphide previously wrapped up in the sulphur, and will dissolve on being treated with mineral acids.

547. *Sulphate of Lead.*—Blackened by sulphide of ammonium. When fused with Na_2CO_3 on charcoal, gives hepar and metal. If recently precipitated, it dissolves in warm solution of acetate of ammonia or tartrate of ammonia. Can be decomposed by boiling with aqueous carbonate of potash, and by treatment with zinc and hydrochloric acid.

548. *Haloids of Silver.*—Blackened by sulphide of ammonium. When recently precipitated, easily decomposed by zinc and water acidulated with sulphuric acid. Under all circumstances completely decomposed by fusion with alkaline carbonate.

549. *Oxides of Tin and Antimony* (if recently formed in wet-way reactions). Soluble in warm yellow sulphide of ammonium. Readily decomposed by zinc and hydrochloric acid with elimination of the metals.

550. *Native Oxide of Tin* (and Tin-Ash).—Rendered soluble by fusion with caustic alkali (in silver crucible); also by fusion with three parts of sulphur and three parts of carbonate of potash (in porcelain crucible).

551. *Tungstic Acid and Tungstates.*—Recognised by blowpipe-tests. (If not disintegrable by hydrochloric acid) may be rendered soluble by fusion with alkaline carbonate.

552. *Titanic Acid.* / *Native Alumina.* } Disintegrable by fusion with six parts of acid sulphate of potash in platinum crucible.

553. *Sulphates of Baryta and Strontia.*—Recognised as Ba and Sr compounds by flame-tests, as sulphur-compounds by hepar-test. Decomposed by fusion with alkaline carbonate.

554. *Fluorides.*—When treated with oil of vitriol in platinum give off HF, which attacks glass. May be disintegrated by treatment with *oil of vitriol* in the heat. Or by fusion with alkaline carbonate and silica. Aqueous extract contains the fluorine, residue the bases.

555. *Silicates.*—Recognised by comportment with microcosmic salt and carbonate of soda beads. Decomposible by fusion with alkaline carbonate; or treatment with fluoride of ammonium and sulphuric acid (in platinum).

556. *Oxide of Chromium.*—Recognised by comportment with borax bead. Dissolves readily in fused mixture of caustic alkali and nitre as chromate, soluble in water. The same method applies to

557. *Chrome Iron Ore.*—The following, however, is a more efficient method: Fuse 2 parts of borax glass with 3 parts of carbonate of potash and soda ($NaKCO_3$), dissolve in this flux ½ part of ore, and heat the fused mass in contact with air for half an hour. The fused mass when treated with water gives up the whole of the chromium as alkaline chromate.—(*W. D.*)

558. *Carbon.*—Recognised by its combustibility into CO_2. Graphite, however, burns only very slowly, even in pure oxygen.

559. *Notes.*—In all the fusion processes above referred to, it is absolutely necessary that the substance should be reduced to an impalpable powder; or else a portion of it will be almost sure to escape decomposition. When we are in doubt as to the proper flux to be used, alkaline carbonate mixed with a little nitre may be used for a first approximation. The fused mass when treated with water gives up to the latter at least part of the acid or acids present, as alkaline salt; the bases remain in the residue in forms which, as a rule, are soluble in acids. 'Alkaline carbonate' means, of course, carbonate of potash K_2CO_3 or carbonate of soda Na_2CO_3; but what works best is the mixture $NaKCO_3$, which fuses far more easily than either of its constituents. Many of those sulphides, arsenides, etc., which are only difficultly attacked by strong nitric acid or aqua regia, readily yield to a mixture of nitric acid of 1·4 and chlorate of potash.—('*Storer's* oxidant.')

560. VIII. *Organic Substances.*

Apart from the methods given in Part III. for the identification of a few organic acids, this book, in regard to organic substances, does not pretend to do more than show how they can be tested for their elementary constituents. But there is no need of our here repeating what was stated: regarding *cyanides* in §§ 470 and 471; regarding salts of oxygenated acids in §§ 478, 481, 487; regarding organic mixtures generally in §§ 490, 491, 492, 493.

Exhaustive Examination of the Salt-Solutions derived from the Substance.

561. In order to complete the analysis of our substance, the salt-solutions derived from it must be examined for the bases and acids which, according to the results of the preliminary examination, can possibly be contained in it. If a *series* of solutions has been obtained, each of these must, as a rule, be examined *separately;* because the way in which the constituents have been separated from one another by the several disintegrators used, always gives some information regarding the nature of the original substance. But even if a mere elementary analysis was contemplated, it *would*, in general, be a mistake to try and save time by mixing the solutions together and analysing the mixture. Such a procedure would not unfrequently lead to the reproduction of insoluble compounds, and defeat the object of previous operations; but even when the solutions can be mixed without the formation of precipitates, the advantage gained by substituting one analysis for the two or more of the separate solutions would be more than outweighed by the difficulties introduced in the former case, through the greater complexity of the mixture.

Examination for the Metals.

562. The methods to be used for the separation of the metals depend on the results brought out in the preceding operations and the degree of potential complexity in the solution. In the sequel we shall consider some cases such as more frequently present themselves in practice. Let us suppose,

563. I. That, from the history of the substance, and the operations which served to convert it into a solution, we knew that this solution could contain nothing but metallic or hydric chlorides, sulphates, nitrates, or other classes of salts exhibiting normal metal-reactions, and that, in particular, we were sure of the absence of (1) combustible carbon compounds, (2) fluorides, (3) silicates, (4) thiosulphates, polythionates and salts of thio-acids (such as As_2S_3, etc.), (5) meta- or pyro-phosphates. This case may safely be left in the hands of the student, as it was fully discussed in §§ 281–293.

564. II. We will now consider the case of, let us say, a purely aqueous solution of *inorganic** *salts*, not sufficiently investigated for placing it into category I. In such a case the first step naturally is to examine the liquid, as far as necessary, for all those classes of acid-radicles, which would interfere with the working of the general scheme of metal-analysis referred to. For this purpose it is generally sufficient to study the action on specimens of the solution, or on the residue it leaves on evaporation to dryness, of hydrochloric acid, nitrate of silver, oil of vitriol, according to §§ 514, 522, 512, 513, and to search for anorthophosphates. These, however, if orthophosphoric acid is present, are sometimes difficult to detect or prove absent. In the worst case we can make sure of their absence by prolonged treatment of the solutum with strong nitric acid, or, what is better, by fusion of the same with excess of alkaline carbonate, when they are bound to pass into the ortho-condition. If one or several of the classes of acids referred to are present, they must be removed by operations guaranteeing the conversion of the metals into such compounds as are accessible to the ordinary methods of separation. The following paragraphs suggest methods for some of the cases that may present themselves:

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* '*Inorganic*' is here taken as including carbonates, cyanides, cyanates, sulphocyanates. Hence the instruction given covers all that can be contained in a solution, obtained by treatment with water of a substance previously exposed to a red heat, and besides includes many compounds which could not be present in such a liquid.

565. 1. *We have to deal with a solution of* **thiosalts.** Such a solution is always alkaline to test-paper. It blackens metallic silver, and gives dark precipitates with nitrate of silver or sulphate of copper. Acidify with *hydrochloric acid* and expel the sulphuretted hydrogen, if formed, by gentle heating. If a precipitate is formed, it may contain sulphur, sulphides of the arsenic group and of mercury; also small quantities of the sulphides of copper and nickel. The filtrate can contain only metals of the barium and potassium and magnesium groups, and perhaps Cr_2O_3 and Al_2O_3.

566. 2. *Alkaline Silicates.*—Supersaturate with hydrochloric acid, evaporate to complete dryness, moisten the residue with strong hydrochloric acid, allow to stand for about a quarter of an hour, treat with water, and filter. Precipitate: *silica*, which must be identified with the blowpipe; filtrate: metallic chlorides.

567. 3. Salts of *sulphur-acids*[*] (others than sulphuric or hyposulphuric) can generally be decomposed by evaporation with excess of hydrochloric acid. Products: sulphurous acid, sulphur, insoluble sulphides, such as Ag_2S, PbS, etc. If such sulphides should separate out, they may either be filtered off and examined by themselves, or destroyed in the mixture by means of some oxidizing agent, such as chlorine-gas, chlorate of potash, nitric acid. On expelling by evaporation the excess of acid and then adding water, we obtain, in general, a precipitate containing, possibly, sulphates of barium, strontium, lead, chloride of silver; and a solution of metallic sulphates, chlorides, nitrates.

568. 4. *Fluorides* must be decomposed by evaporation with oil of vitriol in platinum vessels.

569. 5. *Cyanides.*—These can all be decomposed by being boiled down[†] with excess of hydrochloric acid or by treatment with oil of vitriol in the heat (see § 471). The second method is quite general, but it involves the volatilization or decomposition of almost all the acids that may be present. The following process, which is free from this objection, would probably work in the majority of cases: precipitate the solution with excess of nitrate of silver in the cold, *then* add excess of nitric acid and filter. The *precipitate* contains the *cyanogen-radicles* (NC, $(NC)_6Fe$, $(NC)_6Co$, NCS, etc.); the filtrate contains the metals previously united with these radicles, as nitrates, and, of course, excess of nitrate of silver. Regarding the precipitate, see § 472. The process would not work with cyanide of mercury.

570. A solution containing, possibly, representatives of *all the classes of salts named* could probably be managed as follows: Acidify with dilute sulphuric acid, evaporate to dryness, and heat the residue with oil of vitriol, adding from time to time some nitric acid, until the substance is completely decomposed and oxidized, and all the volatile product (HF, SO_2, CO, CO_2, etc.) expelled. After driving off the bulk of the excess of acid by evaporation, treat with dilute hydrochloric acid and filter:—

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[*] We purposely include the sulphites, as they become troublesome in the treatment of the acid solution with sulphuretted hydrogen.

[†] In a retort connected with a condenser to condense the vapours of hydrocyanic acid.

A. The residue may contain, *inter alia*, silica, [tungstic acid,] oxide of tin (perhaps combined with arsenic or phosphoric acid), insoluble sulphates (of Ba, Sr, Pb), chloride of silver. By digesting such a mixture with sulphide of ammonium,* all the oxides of the arsenic group would be converted into a solution of thiosalts, so that, by filtration, we should obtain,

A *precipitate* containing, possibly, silica, sulphates of Ba and Sr, sulphides of lead, silver, bismuth, etc., and

A *filtrate* containing the arsenic-group metals as thiosalts.

B. The filtrate from *A* could contain only such classes of salts as are accessible to the ordinary methods of metal-analysis.

571. III. *Salts of Oxygenated Organic Acids.*—The only really general method in the case of these is to begin by destroying the organic part by means of some thorough-going process of destruction, such as *Carius'*, treatment with oil of vitriol or nitro-sulphuric acid, etc., so as to obtain all the metals in the form of sulphates, nitrates, or chlorides. But it is not by any means always expedient to resort to such a process of destruction. In many cases the metals can be separated out by the usual group-reagents as used for ordinary mineral salts. It is only necessary to know how far the action of these reagents is liable to be modified by the presence of organic acids.

Silver, *mercurosum*, *lead*, can be separated out as usual by hydrochloric acid, but the precipitate is liable to contain, besides the chlorides of these radicles, also difficultly soluble organic acids such as benzoic, higher terms of the series $C_nH_{2n}O_2$, etc. If such acids should happen to be present, it is advisable to precipitate them by means of some appropriate mineral acid and to remove them by filtration. From the acid filtrate,

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* *Or, if* sulphide of ammonium does not act satisfactorily, by fusing it with sulphur *and alkaline* carbonate, and treating the fused mass with water.

The metals of the *Copper* and *Arsenic Groups* can be precipitated, as usual, by means of sulphuretted hydrogen; only the precipitate is liable to contain, besides these, also zinc, nickel, cobalt, and perhaps even traces of other iron-group metals. From the filtrate of the sulphuretted hydrogen precipitate,

Iron, nickel, cobalt, manganese, zinc, if present, can, as a rule, be completely precipitated by sulphide of ammonium; but aluminium and chromium, especially in presence of non-volatile acids, may escape precipitation. The precipitate is liable to contain insoluble salts of organic acids and barium-group metals, *e.g.* oxalate of lime, etc.

The precipitation of *Barium, Strontium, and Calcium* by means of sulphuric acid and alcohol is not interfered with by the presence of organic acids.

Examination for the Acids.

572. The exhaustive examination of a solution for individual acids, if not accidentally facilitated by accumulation of negative results, may present great difficulties, and even go beyond the resources of analysis. Before entering on such an analysis we must first review the results already obtained and see how far they anticipate or narrow down the problem. The results collected in the preliminary examination, and in the examination for metals, will generally exclude a greater or lesser number of acids as necessarily absent. Thus, for instance, baryta and sulphuric acid, oxide of silver and hydrochloric acid, in acid solutions, and lime and oxalic acid in alkaline ones, obviously exclude each other.

After these preliminaries we pass to the differentiation, first of groups and then of individual acids. On starting, the best system that can be adopted is to successively apply to separate portions of the solution the proper selection of the acid-indicators enumerated in the summary given in §§ 514 *et seqq.*, and with each of these reagents, so to say, to sift out what acids fall within its range, taking care to classify the results according to the *elementary radicles* of the acids found or proved absent, so that a glance at our notes at any moment enables us to see at least how far we have got towards executing an ultimate analysis of the solution. In applying the methods suggested in the summary referred to, we must not forget that much of what it gives rests on the tacit assumption of the absence of those acids which it fails to enumerate, and on the absence also of certain rare combination of substances, not in themselves expressly excluded. Hence a positive result may be owing, not to the respective acids named in the book, but to the presence of some other acids which it fails to take into account; and a negative result, instead of proving the absence of the acid searched for, may be owing to the existence in the liquid of some uncommon combination of things. Thus, for instance, the reaction of barium salts with sulphates even *may* fail, in consequence of the presence of certain pyrophosphates, metaphosphates, or citrates. This source of fallacy is not yet sufficiently investigated. It needs hardly be said that similar sources of error are concealed in our methods for the detection of *bases*, and that the only way to guard against them is not to take for granted any result, whether positive or negative, until it has been confirmed by independent methods of investigation. Apart from exceptional difficulties, we may say that the methods detailed in Part III. will generally enable us to determine the presence or absence of the following individual acids: Hydrochloric, perchloric, hydrobromic, hydriodic, hydrosulphuric, hydrofluoric, sulphuric, orthophosphoric, carbonic, oxalic, silicic, boracic; and of the following *groups* of acids, as groups: oxygenated acids of chlorine lower than $HClO_4$; bromic, iodic; nitrous, nitric; phosphorous, hypophosphorous; the anorthophosphoric acids; a few groups of oxygenated organic acids (besides $H_2C_2O_4$ and H_2CO_3); but the differentiation of the members of a group is possible only in special cases (which, however, in practice are pretty numerous).

Determination of the Acids pre-existing in the Substance.

573. In giving directions (in §§ 543 *et seqq.*) for the disintegration of substances, we had in view chiefly the wants of *ultimate* analysis. How far the solutions prepared are available for the purpose indicated in the heading, depends on the operations employed in making the solutions. It is easily understood that to determine the nature of a substance from the products it yields when operated upon in a given way, is, in general, an indeterminate problem, the more so, the more energetic the action of the reagents used.

A purely aqueous solution, especially if prepared in the cold, can, as a rule, be assumed to contain all the acids and bases of the original substance unchanged. With solutions prepared by means of hydrochloric acid this can no longer be assumed, especially not if the solution was effected in the heat. Volatile acids may have been altogether expelled, others may have been decomposed and the products again may either have been volatilized or remained in the solution. If a solution results from some process of *oxidation* it is, as a rule, available only for a purely elementary analysis. Hence, in the case of a substance insoluble in water, the analysis of the solutions derived from it must, in general, be supplemented by special experiments towards the detection of those of the acids *potentially* present, which, if they had been present, would not have survived the operations involved in making the solutions. Unfortunately there is no general process for extracting in a soluble form, from an insoluble substance, the acids it contains; *sometimes* this can be effected by boiling the finely powdered substance with a solution of carbonate of potash, but the process is by no means generally applicable. In certain cases the quantitative determination of certain of the elements present in the substance may enable one to decide whether it is the one or other of a group of acids which pre-exists in the substance, but this method also is only of limited applicability.

In fact, easy as it is to determine the elementary composition of a substance, *proximate* analysis is, in general, a difficult problem, for the solution of which the science in its present state affords no methods which, even in the most modest sense of the word, could be called generally applicable.

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